REPORTS ON THE PROGRESS OF NAPHTHOLOGY DURING 1926.

Oilfield Practice.*

By A. Beeby Thompson, O.B.E., M.I.Mech.E., M.Inst.M.M., F.G.S. (Member).

Several outstanding features in oilfield practice have been responsible for further acceleration of progress. An advance in methods of surveying wells has led to rather startling and disconcerting disclosures concerning the verticality of deep bores, which, especially in rotary drilling, are liable to deviations of greater magnitude than generally believed. Without doubt these unappreciated deflections of boreholes explain some of the past inconsistencies in results as well as account for some of the pumping troubles. Although the Anderson apparatus enables a true picture of the borehole to be obtained, it is yet far from certain whether means will be found of overcoming this natural tendency to deviation when drilling by rotary in inclined strata of varying hardness. Unquestionably, automatically-controlled feed reduces the chances of deflection through overfeeding when changes of strata are being encountered, but the high cost of the equipment is a factor which is restricting the general employment of such plant.

The general deeper drilling *is*, however, forcing producers more and more to adopt other means of extraction than bailing, swabbing or pumping. Completion of deep, high-pressure wells, under control with regulated flow under pressure, is being more widely practised even where local engineers regarded the outlook as very unpromising. This applies especially to Roumania and Russia, where operators were distinctly prejudiced against systems which restricted the expulsion of sand.

Further investigations are proceeding in many fields on ways and means of controlling the flow of new wells by nipples. This is far from a simple matter where oil is obtained from unconsolidated, Tertiary sediments as in California, Venezuela, Roumania and Russia, when the thickness and exact position of the producing sands cannot be accurately determined. Methodical coring has shown that in many cases oil is drawn from a series of sands separated by clays rather than from a single sand body, and this has led to divergent views concerning the manner of

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exposing the sands to secure maximum output with a minimum of trouble. Some favour perforated pipes, others prefer screens and no general rules can be formulated. There is, however, a disposition to expose a considerable thickness of the oil horizon in deep, expensive wells when conditions admit of this course, and adjust the flow to some amount that keeps the sand influx within moderate limits.

More than ever is it realised that each well is a problem in itself, and on some fields no well is allowed to be completed except under the personal supervision of the production Superintendent or other authorised competent person.

More extended use is being made of air and gas lift for raising oil from deep wells, and it is now largely used in the Mid-Continental oilfields. Great difficulties are met with when endeavouring to pump oil from deep wells after the period of natural flow has ceased, and it is under such conditions that the air-lift can be satisfactorily introduced. In cases like the new Seminole field of Oklahoma, where the volume of gas is not very great and the wells soon cease to flow naturally although the static head remains high, air lift has proved of immense value, as it did in the Baku oilfields of Russia so many years ago.

In June last 325 wells out of 507 producers were using air lift in the Seminole field, the average production per well being about 850 bls. per day. It was considered that the same wells would have averaged by pumping only 216 bls. a day each. The average cost of each completed well equipped with air lift was estimated at $100,000 of which the gas or air lift equipment represented $14,000.

The air lift is being extensively used in the Baku oilfields of Russia, where in May this year no less than 1,300,000 bls. of oil or nearly 30 per cent. of the output was obtained in this way.

It has always been recognised that the use of gas is preferable to air, as it is more soluble in the oil and avoids the adulteration of gas, which may be wanted for gas-gasoline extraction or fuel purposes.

A notable innovation in this direction has been the piping of gas some 30 miles from outside dry-gas areas to the Seminole field for use with gas lifts where there was insufficient gas locally.

Extensive use is still being made of gas lift in California in the deep Los Angeles basin oilfields where so many difficulties were encountered with deep well pumps. A suitably tubed well can be made to flow for years after natural eruption has ended by introducing air or gas, and so assisting the process of lightening the column of fluid; but what is more important, it is possible by the system to retain a pressure on the sands and so diminish the gas

losses. In this way the gas-oil ratio can be reduced from several thousand cub. ft. per bl. to a few hundred. The value of gas as an expulsion agent is being emphasised more and more by technologists, and every effort is being made by the more advanced producers to retard the escape of gas from oil sands. It is frequently observed that the ratio of gas to oil increases as the production of wells falls, clearly indicating that gas is being exhausted at a more rapid rate than the oil, which latter, cores prove to exist still in the sands.

With the increasing importance attached to gas for purposes of production, gasolene extraction and fuel, greater care is being taken to isolate gas sands and preserve their contents for later use when that which accompanies the oil fails to supply requirements after the flush production is off the fields.

Closed circuits for gas lift operations are now in general operation, where the circulated gas is deprived of its gasoline contents during the process of compression. Surplus gas is bye-passed to absorbers and then led to the fuel lines, the treated gas being carburetted during its employment as an expulsion agent. The first plant of this nature was erected in Trinidad years ago, and the gasoline contents paid the whole cost of production. Gas lift has at length been introduced with marked success into the Rumanian oilfields where operators have for years been prejudiced against its employment. Greatly increased yields can be obtained by its use and sand troubles are entirely eliminated. When water has partially flooded the sand, it is the only system that will ensure satisfactory returns.

Considerable attention is now being directed to air, gas and water drives in fields where the settled production barely pays for the recovery of oil. The continued success of the water drive in the Bradford field of Pennsylvania and the Bolivar of New York has led to its extended use elsewhere, but little new has come to light beyond the fact that certain salts assist in disengaging the oil from the sands and increase recoveries. Sodium carbonate has so far proved the best salt for the purpose, but it is yet uncertain whether its use would be repaid by results. The worth of the water drive is indicated by the value of properties formerly having only a salvage value which now command a price of from $1000 to $4000 per acre. The Bradford field now yields 14,000 bls. a day against 5000 bls. a few years ago. Some experiments have been made with a mixed air and water drive with encouraging results, it is claimed, as the air will reach points where water will not. The economic aspect may restrict the application of such work, and in some cases the air may have a deleterious influence on the oil and the equipment.

Air and gas drives are receiving more attention than water drives in America, and many large-scale experiments are in progress or being considered. From the Appalachian oilfields experiments have been extended to the Mid-Continental and Pacific oilfields. Experimental work on the influence of gases on oils has shown that both the viscosity of oils and surface tension are reduced by gas, and that the reductions bear some relationship to the quantity in solution and consequently with the pressure. Further studies on the solubility of various gases in different oils has also confirmed former estimates that oils will absorb about 50 per cent. of their volume of gas, thus bringing the ratio at around 20 atmospheres pressure to about 85 cub. ft. per bl. of oil.

In the application of gas drives to exhausted oilfields difficulties are being found in locating suitable admission centres where neither excessively high pressures are needed nor abnormal losses are occasioned by escape or in by-passing the richer oil streaks. The search for convenient intake wells where a suitable pressure can be built up and held is often undertaken with the aid of a portable compressor. It has been recorded that when air is the medium of pressure restoration the air-gas mixture from the oil wells shows practically no oxygen, but a large percentage of nitrogen and carbon dioxide. The oil likewise increases slightly in density, proving that chemical reactions take place in the sands.

One of the most instructive experiments in hand is that being conducted in the Dominguez field of California, where several large interests controlling the area have combined to test a gas drive in territory where the sands are over 4000 ft. deep. Within a few weeks of admitting air surrounding wells showed a marked improvement.

Of special interest is the fact that vacuum production is being replaced by pressure systems, and it is said that properties which most readily responded to vacuum do so with air or gas drive, whilst avoiding the manifest objections to the vacuum process.

Some little attention has been manifested in the subject of mining oil sands in exhausted fields, but nothing tangible has resulted. There are so many difficulties apart from the question of costs to contend with in most oilfields, that it is unlikely to influence oilfield procedure in most countries in the near future.

Every year more and more care is taken to minimise evaporation losses when once oil reaches the surface. The fact that oil is commonly sold on a gravity basis has been the chief factor in promoting this attitude of producers. It is now customary to run the oil into separators or vapour proof tanks, from which the gas is led away by one main and the oil by another. Storage tanks are protected from the sun's heat by light coloured paints

and shades, and air-fluid surfaces are avoided by using floating roofs or special fluids that spread over the surface of the oi or by breathing devices which inhale or expel saturated mixtures as the level of oil fluctuates. A suitably arranged floating roof with appropriate refinements to provide for deflections of shape of tank, drainage of roof, etc., appears the most effective way of reducing evaporation losses. Foam mixtures are now largely employed for fire protection purposes in large installations.

Two subjects are receiving careful thought in America—viz., Standardization of Plant and Corrosion. The inconvenience occasioned to oil producers by the use of so many sizes and kinds of threadings for tools and casing and specials has long been a subject of criticism from those engaged in oil enterprises. Progress is being made in standardization of plant, and the whole industry will benefit. As regards corrosion of metal under the exposed conditions existing on oilfields, the wastage of iron and steel has been enormous. One American writer has stated that the annual loss from corrosion on the American oilfields reaches $100,000,000 a year.

In the tropics the salvage value of material exposed to a few years' field service is negligible. Not only is there damage due to atmospheric agencies, but the saline waters nearly always associated with oil, as well as corrosive gases, exercise a most destructive action on iron and steel. This particularly applies to well casing, pipe lines and fittings and tankage. Material in use near or in the sea suffer even more, and only partial protection is afforded by paint and galvanising. So far no sufficiently cheap non-corrosive metal has been produced, and reliance has to be placed mainly upon asphalt and tar for outside protection of pipe lines. Tests are being made with asbestos cement pipes, but they are yet unsuitable for high pressures, although they appear satisfactory for low pressure purposes.

A satisfactory way of handling wells yielding very waxy oils has yet to be found. Great production difficulties have been met with in the Panhandle oilfields of Texas, and in Rumania problems of equal perplexity will be met in dealing with the oil from fields drawing the very waxy oils from Meotic strata. The recovery of the dregs of the Yenangyaung field of Burma, the Moreni of Rumania and the Panhandle of Texas will entail some interesting investigations.

Some of the most difficult oilfield problems have had to be faced in developing the Maracaibo Basin oilfields, Venezuela. A great deal of drilling has been done in the lake itself where the water reaches 20 ft. in depth. Heavy rotary rigs have to be built upon piled platforms to which access from the shore is gained by long

piers. Apart from the great expense of these preparations, there is the ever present fire hazard, and the rapid destruction of the piers and piles by the teredo borer which, it is said, renders wooden piles dangerous within twelve months. The use of reinforced concrete piling has been seriously entertained, although the cost would be so high.

Nearly equally difficult has been the task of operating one or two of the Gulf Coast domes situated in swamps. Five miles of raised wooden roadways have had to be built to give access to the Lockport field, Calcasieu parish, Louisiana, where some sixteen wells are yielding 6500 to 7000 bls. a day.

Perhaps most attention has recently been attracted to the subject of restricting output to suit market conditions. Modern drilling methods are enabling wells to be drilled at a rate far in excess of what was deemed possible only a few years ago, and the limits in this respect has not yet been reached. This leads to intensive rivalry and competition, and often compulsory offset drilling in new fields where conflicting interests hold contiguous properties often of small individual acreage. All operators understand that those wells first reaching the oil sands not only secure a great advantage, but usually obtain more than an equitable amount of oil by drawing from neighbouring undeveloped or more leisurely operated plots. In addition, oil is generally deflected towards initial points of relief, and subsequent near-by operations rarely deflect oil from channels once established. These generally recognised facts lead to spirited contests along boundary lines in new fields, with the natural consequence that a glut of oil is produced which has to be put into storage or sold at a low figure to the few owners of outlets. Immense quantities of gas are necessarily lost with their gasolene contents during such irrational development, and fabulous sums are expended in building steel storage for oil which should be left underground safe from all the dangers and losses to which it is exposed above ground. The fact that the cost of steel storage representing about 40 cents per bl. is usually recovered from higher selling values of oil when productions have been stabilised, does not remove the criticism that this constitutes a needlessly high charge on production for which the public eventually has to pay.

Notwithstanding the continual condemnation of present methods, no probable solution of the problem is in sight. The evils attendant upon townsite drilling have been again witnessed at Seal Beach (Alamitos Heights) and elsewhere, whilst Panhandle and Seminole developments have again served to illustrate the troubles that can be brought upon the industry by an indiscriminate scramble

for flush production regardless of consequences. In Rumania heavy losses have been sustained by many operators at Moreni and Runcu, due to the parcelling of the land into so many small plots that only a few lucky ones can possibly reimburse their expenditure. The uncontrolled dissipation of high gas pressures from deep sands must eventually lead to a premature abandonment of fields until some process can be devised for the extraction of the watered dregs.

Attention has been called to the increasing difficulties that are likely to be faced in America by delaying any official action towards pooling oil lands and so promoting rational unit development, due to the increased trading in royalties. It is rightly argued that purchasers of oil royalties retain a perpetual and contingent interest in the oil contents of leased plots which might imperil readjustment of working conditions, especially where many plots and many separate "points" of royalty have been sold broadcast.

Any efforts to control operations in new American fields by mutual consent would appear to come in conflict with the Sherman laws, but where attempted regardless of consequences only partial success has resulted due to a variety of causes. Although the need for the more scientific development of oil pools is generally admitted by which gas could be preserved in the higher parts of domes, and used as a propellant for oil lower down the flanks, where wells could be drilled to suit the peculiar conditions of structure, and water or gas distribution and meet market requirements, no feasible scheme has been propounded, and caution is advised in soliciting Government interference with subjects little understood. Mutual co-operation is guiding the operations on some few structures in California and Texas, where a few wealthy companies share the leaseholds of the district, and in Mexico several of the leading groups have pooled their holdings for organised prospecting. Some fields like those of Salt Creek, Wyoming, Hurghada, Egypt and some East Indian fields have been economically and logically worked by single companies unhampered by offsetting needs, and the results prove the advantage of such a course.

Leasing problems are assuming greater importance in consequence of the increasing employment of gas, air or water drives to extract the oil remaining in the ground when the gas pressure has escaped. Without the mutual co-operation of all producers in a wide area, it is impossible to introduce these methods without causing disturbing consequences.

Drilling Methods and Tools.*

By Ashley Carter, A.M.I.Mech.E. (Member).

The year 1926 has been interesting from the point of view of drilling methods and tools.

The various committees organised by the American Petroleum Institute have continued their activities in investigations, trials and considerations of standards, and considerable advances were made by them during the year.

This year is particularly notable for the fact that the deepest well in the world drilled by rotary or any other system was completed during that period. The well is known as "Olinda 96," and the depth was 8046 feet.

The cost of this well is given by the company concerned, as follows :—

Labour	$67,341·88
Material	110,527·70
Power	8,173·43
Miscellaneous	26,124·02
Total	$212,167·03

The following data has also been recorded, up to August 1st, 1926, only :—

Days all over	516
Working days	487·9
Days suspended	28·1
Days rigging up	8
Days drilling	180
Days fishing and drilling	74·3
Days repairing	20·3
Days running casing	2·6
Days reaming	21
Days redrilling	57
Days circulating	3·6
Days cementing	4
Days testing water	42·5
Days coring	26·6
Days standing cemented	47·4

The casing used in this well was as follows :—

15½ inch cemented at 912 feet.
11 inch cemented at 3600 feet.
8¼ inch cemented at 4691 feet.
6¼ inch cemented at 5595 feet.
4½ inch landed at 8046 feet.

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The well was drilled throughout by electric power. It was surveyed as regards verticality, and the following observations made :—At 6000 feet the well was 517 feet off the vertical, below that depth, at 6948 feet, it swings back to the vertical and is 348 feet off.

A further advance was made in the rotary method of drilling by the scientific and automatic control of the load on the drilling bit. This is accomplished through the agency of a differential, the primary advantage of such a method being that the operation of drilling becomes mechanical after the initial adjustment of the apparatus. The pressure of the bit is automatically increased or decreased according to the softer or harder formation encountered. Provision is made whereby the load on the bit is automatically recorded on a special chart, giving an absolute reading of the work accomplished. Amongst other advantages, twist-off of the drill pipe which has been the principal cause of fishing jobs in rotary drilling is very considerably reduced.

An automatic weight recording device to register the load on the drilling line in the cable tool system of drilling has been introduced. The load is registered on a gauge situated within easy view of the driller, and a graphic record on a chart is also available.

Much attention has been given during the year to metallurgical research in order to arrive at the metals most suited to withstand the various heavier duties resultant on deeper drilling. Alloy steels have received much notice, and one instance is recorded, during the year, of a drilling outfit built entirely of alloy steel, principally manganese. This is comparatively costly when considered in relation to the more regularly standardised forms of material.

Boilers have shown an increase in size—100 horse-power set up in batteries ranging from two, to as many as eight, being frequently installed.

There has been an increase in the size of twin-cylinder drilling engines, particularly for rotary work, and similarly draw works for rotary outfits have been evolved of considerably heavier type than has hitherto been the practice. The drum flanges have been increased and brake rims widened to meet the demands of deeper drilling. Brake drums have been air and water cooled, a new application of this principle so far as rotary drilling is concerned.

There has been a marked advance in the heavier design of the pumps for handling the mud-laden fluid used in the rotary drilling system.

The introduction of the heavier types of drilling rigs has drawn attention to the necessity for improved methods of lubrication, and mechanically-operated lubricators have been widely used.

As motive power, tests have been made with Diesel type drilling engines, the construction being two-cylinder, two-cycle, burning low grade fuel oil. The engines used for the experiments have been of 80 horse-power, with an appreciable overload capacity.

Marked improvements have been brought about in the design of elevators, with movable slips, which, working within a heavy bowl, engage the casing and carry the load.

Anti-friction tool joints and drill pipe collars have been successfully used, the main feature of which is a ring, which prevents the body of the joint from coming into contact with the casing. The ring is separated from the tool joint or collar by ball bearings and rolls on the casing, thereby considerably reducing friction and wear.

Coring has been applied to cable tool drilling, the apparatus consists of a drill barrel, within which as a separate member is fitted a core tube. A vertical reciprocation of the drill barrel drives the core tube over the core of the formation being penetrated.

Retortable Materials.*

By E. H. Cunningham Craig, B.A., F.R.S.E., F.G.S. (Member).

During the past year no very striking advance has been made in the industry of retorting shale and other materials for oil. At the same time experiment and research have been continued, retorting tests on a large scale have been conducted, and the further stage of erecting benches of retorts on a commercial scale has been commenced.

In Great Britain there is not much to record, attention being directed more towards the carbonisation of bituminous coals and slacks, to produce smokeless fuel, either pulverised or in lump, and making tars or tarry oils as by-products, than towards retorting materials primarily to produce oil.

The oilshale industry in Scotland is not yet in a satisfactory position, one mine and two retorting works having been shut down. Under present conditions no rapid improvement is looked for.

Cannel distillation has not yet commenced, though plants are being erected both in England and Scotland to deal with the output of torbanites and cannels at certain collieries. Companies

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to deal with bituminous coal, however, are being projected, but at present only experimental plants on a large scale are suggested.

In Estonia the vertical retorts operated by the Government have proved a failure so far as the quality of the crude oil produced is concerned, while the yield per ton is also lower than it should be. Other forms of retort tried in that country have experienced great difficulty in dealing with the shale, by reason of the plastic stage it passes through in the process of retorting; the very richness of the shale is responsible for many failures to treat it with sufficiently good results.

A serious attempt to treat the oilshales of Bulgaria is being made. That country contains a great quantity of valuable shale, but it will require some years' work before an oilshale industry can be built up.

Very little progress has been made in France, Spain or Italy in developing supplies of retortable material and treating it for oil production.

In Germany the working and treatment of lignites, largely of peat origin, have become very important and profitable, and the extraction of montan wax is carried on on a large scale.

In South Africa, German interests are understood to be considering the utilisation of the torbanites of the Transvaal, but no plant to deal with that rich material has yet been erected.

In Tasmania there is considerable activity in mining and retorting the impure spore coal known as Tasmanite, from which a good yield of oil can be obtained. There have been some difficulties with the retort, but it is understood that these have been overcome. If so, work on a larger scale should soon be commenced.

In the United States of America two forms of retort are being tested in Colorado, by a Government Department, in the great oilshale field. Both are vertical retorts, one being of Scottish type—*i.e.*, a high to medium temperature retort externally heated, and with injection of steam in the high temperature zone. The feed is for all practical purposes continuous. The other retort does not work continuously, and the shale is retorted in batches. It is ignited at the top of the retort, and the products of combustion drawn downwards through the mass of the raw material, thus causing distillation, the oil vapours being drawn out at the bottom. Neither of these retorts can deal effectively with finely crushed material, and they suffer from other disadvantages common to vertical retorts. The results of the tests being made have not yet been published. Both forms of retort should give fairly good yields of oil, and should extract almost all the volatile contents of the shale, but the quality of the crude oil may leave something to be desired.

From the above brief account of practical attempts to produce supplies of oil by retorting methods, it will be seen that the industry in most countries is still in the experimental stage. A very large number of different retorting plants have been invented in recent years, and each has some special advantage, but a retort that will deal with any class of material, that is sufficiently flexible, so to speak, in its working to allow of regulation over a wide range of temperature and rate of throughput, is difficult to find. The nature of the products it is desired to sell has also to be considered, for these may be different for each locality. Thus if ammonium sulphate is required and petrol is not considered as essential, a vertical high-temperature retort is indicated both for shales and cannels, making a crude oil of fairly high specific gravity, and a large volume of uncondensible gas. On the other hand, if petrol has to be considered first, and heavy waxes and ammonium sulphate are of secondary importance, a low-temperature method will be employed, the volatile contents of the raw material will not be quite fully extracted and the yield of gas will be much smaller.

There is no retort known that will give a crude oil of really good quality and at the same time a maximum of uncondensible gas and a large yield of ammonium sulphate.

Among research chemists and engineers the tendency at the present time is to consider the quality of the crude oil rather than to strive for complete exhaustion of the volatile contents of the raw material, the last few per cent. of volatile yielding in any case little more than gas. This reverses to some extent former practice, the idea being that if oil obtained from retorting is to be able to compete with free petroleum, it must approximate as nearly as possible to free petroleum in composition and quality. To put this in other words, it means that the cracking of oil in the retort, with its necessary formation of uncondensible gas and deposit of free carbon, should be kept to a minimum; the crude oil will then contain a good percentage of saturated hydrocarbons. This connotes a low-temperature process, and in order to be able to work quickly and well at a low temperature, the raw material must be crushed finely before being introduced to the retort. The tendency, therefore, is to discard vertical retorts of the old type, which are incapable of dealing satisfactorily with finely crushed material.

Many low-temperature plants of various kinds have been designed, and methods that partake of the nature of extraction as much as of retorting are being tried.

At the same time it is necessary that the process should be simple, cheap to operate and as nearly as possible automatic, while temperature control must be simple and easy.

An elaborate retort that does the work in stages, that requires careful supervision, and contains many moving parts, may make a crude oil of excellent quality, but may be too expensive to erect and operate compared with a more primitive plant.

Again, the locality must be considered: to make a cheap oil cheaply may give better commercial results than to make a much more valuable oil at greater expense. Where raw material exists in enormous quantities the former practice may appeal, where supplies are more restricted the quality of the crude oil produced becomes the most important consideration.

The starting of a new retorting industry in any country requires, therefore, very careful consideration and much experimental work, and it is largely for that reason that progress has been slow during the last year.

Nevertheless, there is a very confident feeling among those interested either as engineers, chemists or geologists that the use of retortable materials for the production of oil is destined to become in the near future of vast importance to the world, that though developments may be delayed in some countries they will be rapid in others, and that finally every source will be exploited and oil formed by "pyrogenesis" will eventually become of greater importance than free petroleum.

Natural Gas.*

By Douglas G. Smith, A.R.C.S., B.Sc., A.I.C. (Associate Member).

Gasoline Extraction Plants.

Many important advances have been made in the perfection of Gasoline Extraction Plants. Of the three well-known systems of extracting the valuable liquid hydrocarbons from natural gas, the original one, that of compression by itself, has been definitely abandoned, since it gives low yields of an extremely volatile product. Also it cannot be said to be selective and requires very high power consumption. Where heavy capital expenditure has already been incurred on compression units, it has been found economical to add a final stripping plant, using one of the more efficient systems of extraction to remove the last traces of gasoline. Since such final stripping plants usually handle a large volume of comparatively lean gas, the charcoal adsorption system has been found particularly applicable.

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The second method of gasoline extraction, known as the gas oil absorption system, has almost become universal, and in nearly every case a pressure of 30 lb. per sq. in. is carried on the absorbers. This pressure minimises the size of plant required without calling for special strength of construction. The design of absorbers, and vertical stripping stills, follows very closely that of other fractionating equipment. Thus the bubble cap plate, and, more recently, the mesh screen or froth type, have been recognised as the most efficient. The screen absorber has been found equal to, or better than, the bubble cap plate column, and is much cheaper and easier to clean. About 35 per cent. of the area of each plate is 30-mesh monel metal wire screen (32-gauge). The absorbent liquid flows across the mesh screen into the down spout to the next plate. No liquid passes through the wire screen, the gas velocity in the upward direction being sufficient to prevent this. By fixing splash plates over the screens, very high capacities with successive plates as near as 8 in. apart are obtainable without priming. The weight of special anti-corrosive metal required is one or two per cent. only of that required for bubble caps. It might be suggested that under low load these absorbers may suffer from oil passing down through the screen against the gas stream. Actually this does not occur in practice, even when running down to as low as 25 per cent. of normal gas velocity. These towers have phenomenally high capacities; thus one 4 ft. diameter absorber, 25 ft. high, operated under 5 lb. pressure, will handle 3½ million cubic feet per day, and under 20 lb. pressure it will handle 5 million cubic feet per day.

Heat exchanger and cooler equipment for gasoline plants has almost reached a stage of finality in the small multitubular type, which has replaced the cumbersome aerial pipe racks so common in the past. The efficiency of an oil absorption process depends to a considerable extent on the temperature to which the absorbent oil can be cooled before entering the absorbers. Above 80° F. the efficiency falls off very rapidly. A refrigerant method has been developed for cooling absorption oil by expansion of compressed and liquefied gasoline vapours. It is claimed that an 80 h.p. compressor using this system will cool 250 gallons a minute of absorption oil through 30° F. A tubular heat exchanger is employed, the tubes through which the oil circulates being completely immersed in the boiling liquid. The refrigerant which may most suitably be a narrow-cut, high-stage compression product, is expanded into the exchanger, the vapours being returned to the compressor.

An important innovation has been the portable type of oil absorption unit. These portable units rated between 2000 and 5000 gallons of gasoline per day, and weighing in all only about

6 tons, can be purchased, already assembled, and can be transported on one truck to the site, and gasoline production commenced in the matter of a few days. The great importance of speed when a new field is opened up, with large volumes of gas going to waste, has made this type of plant very popular. Some of these plants, by working at slightly reduced efficiency, are able to cope with a very heavy overload. During flush production some portable units have actually produced four times their rated capacity.

The third system of gasoline extraction, the charcoal adsorption process, has given satisfaction and extremely high efficiency on lean gases containing no sulphur. It is even in use as a final stripper on some oil absorption plants. Many charcoal plan s, however, have given trouble when operating on gas drawn under vacuum from sulphurous crude oil. Such vacuum collecting lines invariably allow 2 to 5 per cent. air leakage, which, together with the sulphuretted hydrogen, causes the deposition of sulphur in the pores of the charcoal. The charcoal then rapidly loses its adsorptive qualities. Trouble has also been encountered when traces of heavy oil, such as gas oil, have been present in the gas passed through the charcoal. Loss of efficiency in this case can apparently be rectified by reactivating the charcoal with steam at 1100° F.

Stabilisers.

The immense importance of using stabilisers in order correctly to fractionate off all the propane, and other wild gases, is now fully realised, and it is now a very rare exception to find a large plant without an efficient stabiliser. Actually a stabiliser consists simply of an accurate fractionating device to remove the hydrocarbons, which are normally gaseous (and present only in solution) from the remaining normally liquid hydrocarbons. Butane, which has a boiling-point of 34° F. under atmospheric pressure, is on the border line between gas and liquid, and the cut during stabilisation is usually made, leaving most of this constituent in the gasoline. The Rafferty stabiliser consists of a very well lagged bubble plate tower, into which various wild liquid gasolines are introduced at various heights, according to their composition. These wild liquids are led to the tower under pressure and pass through control valves on to the desired plate. The sudden drop in pressure at these valves causes violent ebullition, and the latent heat of evaporation is used to maintain a very low temperature at the top of the tower. The pressure on the tower is usually about 5 lb. per sq. in., and the temperature of the vapours leaving the top is usually minus 15° F. This stabiliser will increase the yield of saleable gasoline, obtainable from the average gas oil absorption

plant, by about 15 per cent., and from straight compression plants by a still greater percentage. The power required for recompression, however, is rather high. An oil absorption plant producing 40,000 gallons a day, and fitted with a Rafferty stabiliser, requires about 400 h.p. for the recompressors.

Another stabiliser, equally efficient in operation, is maintained at about 200 lb. per sq. in. and at 100° F. at the top of the tower. The wild gasoline to be stabilised is pumped through heat exchangers and into the tower about a third of the way up, its temperature on entering the tower being about 150° F. The hot stable product from the still at 230° F. passes away through the exchangers, and some final coolers, to storage. The vapours from the top of the tower pass into a reflux condenser. The vapour leaving the reflux condenser passes through a back-pressure valve and is free from liquid fractions.

While normally a gasoline stabiliser is only required to separate two products, that is wild gases from stable gasoline, it may be extended to produce practically pure fractions of the lower hydrocarbon members, so that 90 to 95 per cent. pure ethane, propane, butane and pentane can be secured on a commercial scale. This is of great importance in the production of more valuable chemical derivatives. By subjecting these gases to a cracking process in ferrochrome tubes the corresponding olefins are produced, from which such valuable products as dichlorethylene, ethylene glycol, ethylene chlorhydrin, isopropyl alcohol, acetone, dimethyl ether, etc., are being produced.

Gas Lift.

A very important advance during 1926 has been the perfection of a successful system of gas lift. This system obviates the pumping of crude oil wells and greatly increases the production of oil and, incidentally, casinghead gasoline. One company has six areas on this system, and in each case the production is more than double that of the surrounding wells in the same sand. The gas to oil ratio is materially reduced in all cases by using the gas lift. The average reduction of this ratio is from 53 cu. ft. per gallon to 34 cu. ft. per gallon of oil. This is regarded as a very important step in the conservation of oil resources. Briefly the gas lift system consists of first stripping the gas of gasoline by gas oil absorption, compressing the stripped gas to 300 lb. per sq. in. and injecting it into the bottom of the well. The gas is usually admitted to the well between the tubing and the oil string. It enters the tubing at the bottom, and lifts the oil to the surface. The amount of gas circulated per well varies from one-tenth of a million up to 1½ million cu. ft. per day. One section of 15 wells,

for example, producing 150,000 gallons of crude per day, has a total of 8 million cu. ft. of gas circulated, and the total gas production is 12 million cu. ft. This means that 4 million cu. ft. of new gas is produced per day, that is 27 cu. ft. per gallon. The 12 million cu. ft. of gas separated from the oil at the well head in this case contains 2 gallons of gasoline per 1000 cu. ft. Thus 24,000 gallons of gasoline are produced per day.

The average increase in oil production taken from several hundred wells operating on gas lift is over 60 per cent. The amount of gas used in different areas varies very greatly. Thus, anything from 12 to 85 cu. ft. per gallon are being used, and as the average cost of compression to 300 lb. is 2d. per 1000 cu. ft. the compression costs amount to 6d. to 3s. 6d. per ton of crude produced. This, however, is frequently less than pumping costs. It has been found in actual practice that some wells hold up their production on this system at a constant rate for as long as two years. The gas lift system scientifically applied is therefore becoming recognised as an efficient substitute for pumping.

Chemistry.

By H. B. Thompson, M.Sc., Ph.D., F.I.C. (Member).

The question of the origin of crude oil does not appear to have received a great deal of attention during the past year, judging by the paucity of published work on the subject.

Clarke[1] considers it to be due to the action of anærobic bacteria on marine animals and plants.

Possibly the most outstanding feature of the period under review is the large amount of research being carried out in connection with the isolation and identification of the naturally occurring compounds in petroleum.

Seyer and Huggett[2] identified some dozen hydrocarbons from $C_{10}H_{20}$ to $C_{19}H_{38}$ from a 150/350° boiling point fraction of Peruvian petroleum.

Vesper[3] describes a method of distillation analysis of petroleum with special reference to Southern Californian crude oils.

Danaila[4] determines the aromatics by 98 per cent. sulphuric acid and the unsaturated hydrocarbons by means of ozone in various distillations from Rumanian oils.

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[1] *Journ. Inst. Petr. Techn.*, 1926, **12**, 257.
[2] *Trans. Roy. Soc. Canada*, 1926 (iii), 20, III, 193.
[3] *Ind. Eng. Chem.*, 1926, **18**, 64.
[4] *Petroleum*, 1926, **22**, 209.

Sachanov[5] quotes the percentage yields and some constants of fractions of the four types of oil from the Grosny fields.

Mabery[6] separated two series of compounds, D. hydrocarbons (lubricants) and H. hydrocarbons (asphaltic oils), by fractional extraction with ether and alcohol of Mid-Continent crude and lubricating oils. Molecular weight determinations showed that the series C_nH_{2n-4} and C_nH_{2n-8} are the best lubricants; those poorer in hydrogen show asphaltic properties. Marked differences were observed between the refractive indices of the D. and H. series, he former having the higher index. Viscosities of the fractions were determined in Ostwald tubes, and the resistance of films of the oils to stress in a hard Babbitt-metal bearing.

Neubronner[7] describes the properties and constants of oil obtained from Holzheim shale.

Carpenter[8] has published a paper on petroleum fractions from Burmah crude and other petroleum sources, and on the standardisation of the aniline C.S.T. method for kerosine fractions. It deals with the quantitative and qualitative determinations of aromatics, naphthenes, paraffins and other hydrocarbons in all fractions boiling below 300° C. by C. S. T., refractive index, specific gravity and chemical tests with the aid of fractionation, fractional solution at varying temperatures in solvents such as aniline or O-toluidine and other physical and chemical means. The author has dealt with his subject in a masterly manner, and any attempt to abstract or condense the paper into the short space available would give no idea of the enormous amount of work that the author must have done.

He has also published a paper on "The Physical and Chemical Properties of Paraffin Wax from Burmah Crude,"[9] in which he shows results which point to the presence of the complete range from $C_{21}H_{44}$ up to $C_{34}H_{70}$. A pure hydrocarbon of m.p. 96.5° C. has been obtained, the formula of which is probably $C_{57}H_{116}$, and this is believed to be the highest member of the paraffin series yet isolated from a purely mineral wax.

H. I. Waterman and Perquin[10] contribute to the knowledge of polymerisation, and have carried out a systematic research on the action of porous substances on unsaturated hydrocarbons.

Wilson and Schnetzler,[11] in a paper on the effect of pressure and

[5] *Chem. Z.*, 1926, I, 2269.
[6] *Ind. Eng. Chem.*, 1926, **18**, 814.
[7] *Petroleum*, 1926, **22**, 57.
[8] *Journ. Inst. Petr. Techn.*, 1926, **58**, 518-567.
[9] *Journ. Inst. Petr. Techn.*, 1926, **56**, 288-315.
[10] *Journ. Inst. Petr. Techn.*, 1926, **58**, 506-517.
[11] *Ind. Eng. Chem.*, 1926, **18**, 523.

temperature on the total volume of partially vapourised Continental crude, state that the shape of the curves obtained by plotting the results indicates solubility of water in the oil. At moderate pressures and temperatures above 150°, the volume of vapour produced is so large that it must be allowed for in calculations concerning design of rectifying stills.

The question of detonation, and inducers and suppressors thereof, has not claimed as much attention as would have been expected.

Clarke, Brugmann and Thee repeated the experiments of Wendt and Grimm on the rate of recombination of gaseous ions. Mixtures of air, benzene and butyl nitrite, and of air, benzene and lead tetra-ethyl were ionised by exposure to monochromatic X-rays, and the ionisation measured at 2 points about 20 cm. apart in a secondary ionisation chamber. The ratio of the ionisation currents at the two points gave a measure of the relative rates of recombination of the ions. The presence of the butyl nitrite slightly increased the total ionisation of the benzene-air mixture, and slightly decreased the rate of recombination. This is in accord with the theory of Wendt and Grimm. The presence of lead tetra-ethyl gave a still larger total ionisation and a greater decrease in the rate of recombination. This accords neither with the theory nor with the results of Wendt and Grimm. The above results were confirmed by a second series of experiments using a specially designed and very sensitive ionisation chamber and quadrant electrometer. The theories that have been suggested to explain the action of knock suppressors are summarised.

Muraour[12] suggests that the action of anti-detonators such as lead tetra-ethyl in internal-combustion engines is due to the formation of a cloud of solid particles which fix a proportion of the ions in the gas and thus moderate the rate of explosion. The fact that benzene-air mixtures can be strongly compressed without detonation is ascribed to initial combustion of the hydrogen, whereby a cloud of carbon particles is formed and acts as an anti-detonator.

Ferrari[13] quotes a method for the determination of lead tetra-ethyl in motor fuel which has given very accurate results.

Clarke and Thee[14] studied the spectra of detonation flames in an internal-combustion engine, and found that the characteristic banded structure was readily distinguishable from the spectra of explosion and combustion. Characteristic lead lines were prominent when lead tetra-ethyl was used and the ultra-violet region was shortened. Butyl nitrite (a detonation inducer) accentu-

[12] *Chim. et Ind.*, 1925, **4**, 851.
[13] *Giorn. Chim. Ind. Appl.*, 1925, **7**, 625.
[14] *Ind. Eng. Chem.*, 1926, **18**, 528.

ated the ultra-violet spectrum. The study of the spectra of the flames in the internal-combustion engine promises to be a satisfactory method of elucidating the reaction mechanism under varying conditions.

Ormandy and Craven[15] examined a spirit derived from the Berginisation of Orgreave washed slack. By a long series of fractionations, determinations of refractive indices and iodine values and preparation of nitro derivatives of the aromatic compounds present, a large number of hydrocarbons was definitely identified.

Brooks[16] describes further work on the colour and the resinifying and gum-forming properties of petrols and cracked light oils. The olefines on atmospheric oxidation form peroxides which break down to give aldehydes (including formaldehyde), ketones, water, CO_2 and simple organic acids. The peroxide and liquid aldehydes and ketones form fluid gums, but the resins are acidic—not aldehydic compounds. Small proportions of easily oxidisable hydrocarbons, such as diolefines (particularly if they are conjugated) promote the formation of much gum. Ordinary olefines give gum more slowly. Traces of acidity cause the discolouration of petrols and paraffins, and are due to sulphur-dioxide, its oxidation to sulphuric acid, and the oxidation of mercaptans and alkyl disulphides. Alkalis, oil soluble bases and steam (owing to its solvent action) may prevent this type of discolouration.

Waterman and Blaauw[17] obtained a gasoline boiling up to 150° from the action of hydrogen at 450° and pressures of 280/290 atm. on Rangoon paraffin wax. Careful fractionation indicated that the gasoline contained large quantities of the successive members of the paraffin series (*n*-pentane to *n*-nonane) and probably a small amount of olefines (about 10 per cent.). Benzene was not detected and toluene was only present to a very small extent.

Sachanov and Bestuschev[18] examined a number of samples of protoparaffins from Grosny petroleum. The solubility of these samples in light benzene, machine oil, benzene and isoamyl alcohol was investigated, and the results are given in tables and graphs. The protoparaffins dissolve as true crystalline substances, and there is no difference between them and pyroparaffins, observed differences of behaviour being due to the accompanying substances in crude oils and residues.

Padgett, Hefley and Henricksen[19] have studied the question of

[15] *Journ. Inst. Petr. Techn.*, 1926, **12**, 77.
[16] *Ind. Eng. Chem.*, 1926, **18**, 1198.
[17] *Rec. trav. chim.*, 1926, **45**, 284.
[18] *Petroleum*, 1926, **22**, 484-486.
[19] *Ind. Eng. Chem.*, 1926, **18**, 832.

crystallisation of various paraffin waxes from solution in oil. Three types of crystallisation were detected—viz., very small crystals from residual oils and petroleum, fine needles from slack wax and ordinary paraffin wax, and plate-like crystals produced in small numbers during the initial crystallisation of paraffin wax, and also deposited between the above-mentioned needles on keeping for some time.

Leslie and others[20] determined the latent heats of vapourisation of a series of narrow boiling-range fractions from a high-grade paraffin base oil. The latent heats observed were for fractions boiling at 66·5°, 142·4 B.Th.U. per lb.; at 148·8°, 117·4 B.Th.U. per lb., at 232·2°, 92·2 B.Th.U., and 315·5°, 67·1 B.Th.U. The determined latent heats at the higher temperatures fall well below the values calculated by Trouton's rule.

Kita Abe and Tada[21] investigated the action of ozone on the saturated hydrocarbons of petroleum. By the action of ozonised oxygen, containing about 5 per cent. ozone, on a fraction (b.p. 150-300°—mainly saturated hydrocarbons) of Kurokawa petroleum, the iodine and acid values, specific gravity, refractive index and viscosity increased to an extent dependent on the time of treatment, while the rotary power decreased. In the case of liquid paraffin (Jap. Pharm. iv.) the acid value, specific gravity and viscosity increased slightly, while the rotary power decreased.

Catlin[22] obtained ·007 per cent. of phenols from cracked spirit by washing with caustic soda. The oil was precipitated from solution by H_2S from still gases. The phenol fraction distilled mainly between 195° and 227°; it gave tests for cresylic acid but contained no cresols. Its density was 0·995 to 1·013.

Birch and Norris[23] have isolated a considerable number of benzene and naphthaline derivatives from the acid tar obtained in refining Persian kerosine. A satisfactory method for the identification of aromatic hydrocarbons is to replace all the nuclear hydrogen atoms by bromine, with subsequent examination of the crystalline bromo-compounds.

Schmidt[24] attributes the corrosion in condensers to the hydrogen-sulphide evolved from the oil and also to hydrochloric acid from the magnesium chloride in the water which accompanies the oil; no satisfactory resistant alloy has been found. Nickel-chrome or rustless steel and block tin gave the best results, and wrought iron

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[20] *Ind. Eng. Chem.*, 1926, **18**, 95.
[21] *J. Soc. Chem. Ind. Japan*, 1926, **29**, 7.
[22] *Ind. Eng. Chem.*, 1926, **18**, 743.
[23] *J.C.S.*, 1926, 2545.
[24] *Petroleum*, 1926; **30**, 1139.

and steel the worst. The risk of corrosion by H_2S in cracking plants at high temperatures is mentioned.

Wood, Sheely and Trusty[25] have investigated the action of various refining agents on naphtha solutions of pure organic compounds. The refining agents used were sulphuric acid (fuming, d. 1·84 and d. 1·58), sodium plumbite, sodium hydroxide, silica-gel, fuller's earth and alumina. Stock solutions of sulphur derivatives (iso amyl-mercaptan, hydrogen sulphide, methyl sulphate, methyl *p*-toluenesulphonate, carbon disulphide, *n*-butyl sulphide, *n*-propyl disulphide, thiophen, diphenylsulphoxide, *n*-butyl sulphone, and free sulphur) were made in a sulphur-free petroleum distillate $d^{20}/0{\cdot}77$. The general procedure was to treat 50 c.c. of the stock solution with two quantities of the reagent (4 and 16 c.c. respectively) for a period of 1 hour, the desulphurising efficiency being measured by the decrease in sulphur content after treatment. Under these conditions, H_2SO_4 of all strengths was quite ineffective to free S or to CS_2, but the other sulphur compounds were removed fairly easily, except in the case of the weaker acid. Sod. plumbite removed H_2S and alkyl sulphate and to a certain extent the mercaptans as lead mercaptide. Sodium hydroxide behaved similarly to sod. plumbite. Silica-gel was effective in most cases except free H_2S, CS_2 and thiophen. Fuller's earth and alumina behaved similarly and were less effective than silica-gel. The action of the last three agents is due to adsorption only: the effects of each agent on each sulphur compound are tabulated.

Wood, Greene and Provine[26] have carried out work to ascertain the desulphurising effect of sodium hypochlorite on naphtha solutions of various organic sulphur compounds. These latter comprised ethyl sulphide, *n*-butyl sulphide, phenyl sulphide, ethyl-disulphide, *n*-propyl sulphide, ethyl mercaptan, *n*-propyl mercaptan, iso amyl mercaptan, CS_2, H_2S, thiophen and elemental sulphur. The effect was found to depend on the actual sulphur compound used, the amount of available chlorine present, the degree of alkalinity of the hypochlorite solution, and the time and intensity of agitation. Thiophen and elemental sulphur are not attacked by sod. hypochlorite; the aliphatic sulphides vary in the ease with which they are oxidised to sulphones. The disulphides are somewhat less readily attacked than the sulphides, and the mercaptans still less readily: H_2S is oxidised to elemental sulphur and CS_2 is partially removed. The conversion of the sulphides into sulphones is beneficial in refinery practice, as the latter compounds are more easily removed from the naphtha by subsequent treatment,

[25] *Ind. Chem.*, 1926; 18, 169.
[26] *Ind. Eng. Chem.*, 1926, **18**, 823.

redistillation and filtration through an adsorbent material. Better results in general are obtained by using hypochlorite solutions comparatively rich in chlorine and alkali rather than solutions weak in these respects. In designing a suitable hypochlorite treatment for a particular naphtha, a careful study must be made as regards the oxidation products : if these are acidic, then sufficient alkali must be present initially to maintain a final alkaline solution.

A paper has been published by Dunstan and Clarke[27] on the general properties of lubricating oils and their practical application. The authors show that the substances of real value are those which possess to a marked degree the property of "oiliness," or the ability to form a coherent slippery film between opposing surfaces, the bodies possessing this characteristic being animal and vegetable oils and the heavier or higher boiling point fractions of petroleum. The number of these latter is very large and knowledge of their composition very incomplete. They consist of hydrocarbons of different series and, whilst some slight knowledge has been acquired of the principal series of hydrocarbons occurring in the lubricating fractions which are obtainable from crude oils from different fields, but little is known of the quantitative composition of these oils, and less of their chemical constitution. In general, lubricating oils from petroleum are complex mixtures containing only a small proportion of paraffin hydrocarbons of the formula C_nH_{2n+2}, and consisting chiefly of hydrocarbons whose formulæ range from C_nH_{2n} to C_nH_{2n-8}. A few of these compounds, whose molecular weights range from 304 to 1700, have been isolated by Mabery from American crude oils.

A brief description is given of the manufacture of lubricating oils from petroleum, together with interesting notes on the nomenclature of lubricating oils. A summary of the physical properties show that *Specific Gravity*, although relatively unimportant from the point of view of actual lubrication, is a constant that must be known to determine weight-volume relations and to deal with certain other physical properties adequately ; low specific gravity together with good demulsibility being a desirable characteristic for turbine circulation and enclosed steam engine oils. *Flash Point* is important as an indication of readily volatile material which an oil contains, giving a measure of possible fire risks. *Viscosity* affords valuable information as to the suitability of the oil for particular duties ; in fact, it may be regarded as the most significant property in ordinary specifications : nevertheless, viscosity is not a measure of the real "oiliness" of an oil. *Pour Point* affords information as to the temperature to which an oil may be cooled

[27] *J. Soc. Chem. Ind.*, 1926, **39**, 690.

and still remain fluid, and is dependent upon the quantity of paraffin wax dissolved in the oil. *Surface Tension* of an oil (which is nearly related to surface energy) is most probably an important factor in lubrication.

A summary of the chemical properties shows that inorganic *Acidity* should on no account be present in an oil. Free fatty acids are only present in compounded oils. Petroleum acids are very weak and do not affect bearing metals appreciably. *Saponification Value* is valuable as a measure of the degree of compounding (*i.e.*, addition) of fatty oils. Carbon residue is usually determined, but, so far as the authors are aware, no exact relation has been established between the carbon deposit on the cylinder heads and pistons of an internal-combustion engine and the carbon residue value of the oil in use. *Iodine Values* afford some information regarding the proportion of unsaturated substances present in the oil. *Oxidation, gumming or tendency to sludge.*—The resistance of an oil to oxidation is of very great importance for many classes of oil, particularly those which are exposed to high temperature and come in contact with air. All commercial oils possess, to a greater or lesser extent, this tendency to oxidation or sludging, unless very specially refined. *Demulsibility.*—The tendency of an oil to form more or less permanent emulsions with water is of obvious importance in cases where the oil comes in contact with wet steam. For oils used in bearings and internal-combustion engines, good demulsibility is of minor account. Latent period and mixtures of lubricants, and heat of absorption of oils, are also dealt with.

Hackford[28] also deals with some characteristics of lubricating oils.

Erskine[29] estimates the aromatic hydrocarbons in gasoline by means of nitro-benzene instead of aniline. He claims that the advantages of the method are the lower temperature employed and the degree of accuracy (+ ·2 per cent.) obtained.

Brown and Carr[30] prepare pure hydrocarbons from commercial gasoline produced in the Cabin Creek Field, by the use of simple fractionating columns without analysers, and have obtained excellent results.

Frances and Gauntlett[31] investigate the complex non-acidic derivatives found among the products of air oxidation of paraffin wax at 100° C. The authors prove the presence of secondary alcohols and ketones, and show that dihydroxy alcohols, hydroxy-ketones and diketones are probably present.

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[28] *J. Soc. Chem. Ind.*, 1926, **39**, 694-697.
[29] *Ind. Eng. Chem.*, 1926, **18**, 694.
[30] *Ind. Eng. Chem.*, 1926, **18**, 718.
[31] *J.C.S.*, 1926, **36**, 2377.

Refining and Refineries.*

By J. McConnell Sanders, F.I.C., F.C.S. (Member).

General.

The year 1926 will be regarded historically as one of exceptional activity in all branches of petroleum industry.

The total production of crude oil was larger in volume than in any previous year, although the order of achievement amongst the productive countries was somewhat different in arrangement.

Mexico, although still second to the United States showed a decline of over 2 per cent. compared with her contribution in 1925, while Russia, as third in order of productive merit increased her 1925 quota by nearly 30 per cent.

Altogether out of twenty-five producing countries, thirteen showed an increase over their 1925 production, ten decreased, while in two the production was substantially unaltered.

In the United States the production reached the record-breaking total of over 770,000,000 barrels and according to G. R. Hopkins[1] the year under review was characterised by a steady increase in production, the daily average for each month being greater than that of the previous month.

The outstanding features of the year in the United States were the discovery and development of the Seminole Field in Oklahoma, the Seal Beach Field in California, and the rapid development of the Panhandle Field in Texas, the nature of the oil found in the latter region introducing some new problems in refining practice owing to the nature of the sulphur compounds contained therein.

Venezuela and Columbia showed a remarkable increase in productivity, the former sharing with Persia the fourth position amongst the world's producers, having almost doubled its 1925 production, while the latter, although contributing only 0·4 per cent. of the total, yet actually produced 7¼ times as much oil as it did in 1925.

The crisis in Mexico brought about by its present Government's attempt to enforce confiscatory provisions in legislation governing oil production, may to some extent be regarded as a causal factor in curtailing activity there, but apart from this there was a steady decline in production month by month throughout the year in spite of the efforts of several optimistic companies to tap new productive fields. It would seem that unless some untoward event happens to arrest the phthisical symptoms in the Mexican petroleum organism

* Paper received April 30, 1927.

[1] *Oil and Gas J.* **25**, 43, 68.

the centre of activity immediately south of the Rio Grande will shift to the other side of the Panama Canal.

It is natural to expect that the effect of flush production in crude oil would be reflected unmistakably, not only in the world's markets but also in the world's refineries, and especially in those centres where increased crude supplies were unexpected and consequently unprovided for.

A somewhat similar condition existed in 1923 when California was unable to refine all its production, and eastern refineries of the United States and even some Mexican installations found it worth while to charge their stills with Californian oil.

In the Seminole district the congestion is being met by enormous increases in pipeline facilities, but in spite of all efforts to redistribute the crude among areas capable of refining it with profit, the crude oil price level is so low that an increase in storage capacity is foreshadowed in many regions rather than any additions to present refining facilities.

Nevertheless, the statistical barometer for refinery activities in the United States showed a rising tendency throughout the year and to all appearances is still at "set fair."

According to the preliminary reports of the Bureau of Mines, the crude oil run to stills in 1926 was 42,641,000 barrels, or 5·8 per cent. more than in 1925, while the proportion of gasoline recovered averaged 38·3 per cent. as compared with 35 per cent. for the previous year.

It should be pointed out, however, that the crude oil refined was on the average of lighter quality, and according to one authority[2] the year was the first since 1918, in which the demand for gasoline has kept abreast of production.

According to G. R. Hopkins[1] the production of gasoline was 15·5 per cent. more than in 1925, and of this, 31·3 per cent. was produced by cracking, the latter fact being reflected in the corresponding production of gas oil and fuel, which in spite of the increased quantity of crude run to stills, was not greatly in excess of the 1925 production.

It is interesting to note that concurrently with the high level of refinery activity maintained in the United States, the situation in other countries has shown anything but a retrograde tendency.

A report published in June of last year[3] stated that the refinery at Barranca Bermeja in Columbia handled something over 500,000 barrels of crude in 1925, the capacity being about 2,500 barrels daily.

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[2] *Oil Paint and Drug Reporter Market Rev.* **3**, 5, 98.
[3] *Oil and Gas J.* **25**, 4, 128.

In Venezuela it was reported that the Lago Petroleum Co. in addition to their topping plant at Salinas, was constructing a refinery on Aruba Island, while the Royal Dutch refinery at San Lorenzo was being enlarged to accommodate more than its then stated capacity of 700,000 barrels per annum.

In Peru the principal refinery is operated by the International Petroleum Co. at Talara, while F. Piaggio & Co. have a small refinery operating at Zorritos.

Refining in Ecuador is represented by the small but modern installation at Santa Elena owned by the Anglo-Ecuadorian Oilfields, Ltd., and also by several smaller plants.

In the Argentine Republic, apart from the Government refinery at La Plata, there are five others with an aggregate daily capacity of about 50,000 barrels. The Government plant is reported to have a daily capacity of some 14,000 barrels, but early in the year increased its plant by the acquisition of two Cross-cracking units.

The above-mentioned refineries in South America have been referred to with the object of indicating the general tendency for refinery activities to move southwards and in the direction of new oilfield developments, it is outside the scope of the present review to attempt to survey in detail every centre of the world's activity, but brief mention should be made of some important developments in Europe, as indicative of changing conditions there.

In Russia, for instance, there were well marked indications that the refining industries were awakening from the comatose condition produced by the Great War, and the hectic political situation which followed it, in fact Russian refined products reappeared in the world's markets, and their volume is still increasing.

In Great Britain the growth of the refining industry has been remarkable and according to the *Board of Trade Journal* is indicated by the figures for imports of crude oil, which from one million gallons in 1913 rose to 7½ million in 1919 and after dropping to four million in 1920 rose again suddenly to 101 million gallons in 1921, increasing steadily to 569 million in 1925, with a slight decrease in the 1926 figure which totalled 539 million gallons.

In the year under review it is computed that 1½ per cent. of the world's production was refined in Great Britain, the main source of the raw material being Persia, although considerable quantities of crude oil were brought in from Venezuela, Mexico, Columbia and the United States, while Trinidad and Sarawak contributed a little over two million gallons.

It is pointed out by the Board of Trade publication that the quantities refined in any year are not necessarily the same as the importations in that year, and, moreover, the Customs returns for crude

oil do not include other varieties of raw material such as kerosine from Rumania and Russia, which was used for cracking.

The total output of liquid products from refineries in Great Britain including cracking plants, was 554 million gallons plus asphalt, pitch and wax. These were derived from about 576 million gallons of petroleum of which 80 per cent. was crude oil, about 15 per cent. semi-refined oil, and 5 per cent. was kerosine. There was also about 40 million gallons of oil and naphtha derived from shale retorting.

A further point of interest as regards Great Britain is the fact that of the 677 million gallons of motor spirit retained for consumption and replenishing of stocks (which had fallen during 1925), 20 per cent. were manufactured in the country, which was 6 per cent. lower than the corresponding figure for 1925. Kerosine and fuel oil also showed some falling off from the 1925 figures as regards the percentages of total consumption represented by home manufacture, the figures being respectively 18 per cent. and 35 per cent. as compared with 33 per cent. and 42 per cent. for 1925.

Rumania showed a remarkable recovery in refinery activity from the immediate post-war conditions, the situation being considerably helped by agreements entered into between the British, French and Rumanian Governments with respect to claims for compensation made by the two former countries for properties destroyed during the war for defensive purposes.

Refinery Plant and Equipment.

A survey of the literature for the year 1926 does not reveal many outstanding novelties or radical departures from conventional types of refinery appliances. There have been numerous suggested improvements to stills, fractionating devices and condensing equipment, but many of these are adaptations from kindred and older industries, while others reflect simply the existence of local problems dependent upon special conditions, there is nothing to report which would merit the designation "revolutionary."

In horizontal still design some attention has been directed in the United States towards the so-called "through-fired" type with internal flues, but the familiar European model with two large flues about 3½ feet in diameter, has been substituted by one with a number of 4 or 6 inch tubes.

In a paper read by B. N. Broido before the American Society of Mechanical Engineers at San Francisco last June, the author dealt with the general problems of heat transmission and makes out a case for a method of generating steam by installing water pipes in the furnace of the ordinary tubular still.

The disadvantages of intermittent or batch distillation, more especially in the case of lubricating oils, are well known to all refiners, and were specially dealt with by W. F. Parish in a paper read before the Franklin Institute at Philadelphia, where he described the Zieley vacuum still in which the oil is continuously preheated and delivered to a specially designed separator maintained under a high vacuum, whereupon the oil is said to "flash into vapour" to the extent of about 25 per cent.

Improvements in method and apparatus for distilling oils under vacuum are claimed by R. Neumann and L. Steinschneider in a recent patent[4] wherein it is pointed out that in a vacuum still fired from below the actual pressure at the heating surface may be as much as 100 mm, owing to the height of the column of oil, although the vacuum gauge only registers 5 mm. The authors propose to eliminate cracking of the oil due to this higher pressure and consequent higher boiling temperature, by pumping the oil from the bottom of the still into trays situated above the oil level, where conditions are so adjusted that vaporisation only takes place in the trays, the unvaporised portion overflowing and running back into the still.

A somewhat novel form of still has been patented by J. M. Sims and O M Brooks[5] who describe a large heating coil made of bolted steel tubes lined with clay which are transversed at intervals by a continuous coil, the bends of which pass through the walls of the heating coil and can be removed if necessary.

C. M. Alexander[6] claims some advantage in a method of injecting steam at various points in a pipe still, and maintaining oil and steam in intimate contact.

The well known inventor of the Trumble still is responsible for three more inventions relating to the art of distilling oil. In one[7] an arrangement is described whereby oil heated to a desired temperature is delivered to a separator, the discharge from which is regulated in proportion to the feed by means of a special device.

In a second[8] an evaporator is described which comprises a cylinder rotating on a shaft projecting from each end, and supported on bearings. The cylinder is surrounded by a thin-walled casing, and oil is fed into the cylinder while oil and vapour are withdrawn from the casing. The bearings are electrically insulated from the casing and an E.M.F. is maintained between the ends of the cylinder.

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[4] E.P. 257,257.
[5] U.S.P. 1,581,879.
[6] U.S.P. 1,585,224.
[7] U.S.P. 1,586,130.
[8] U.S.P. 1,586,132.

The third invention[9] refers to a form of continuous refluxing still in which a coil installed within a chamber receives the condensate from a condenser. Surplus liquid from the coil chamber is returned to the still, while vapours proceeding from the coil chamber are condensed separately.

A still and reflux condenser is also described by F. M. Floyd[10] the arrangement comprising a coil placed inside the reflux condenser the lower end of the latter communicating with the still. The oil to be distilled enters the condenser at the top, passes down a tube to the bottom of the coil and leaves the top of the coil by a pipe which passes through the bottom of the condenser and leads to the still.

In a topping plant described by C. F. Hanson and P. Vandervort[11] a vertical oil passage is fitted with a number of convex plates which tend to divide the oil into two streams, while outlets for vapours are provided above each plate.

A variation in the conventional type of tray still is provided by a design patented by F. M. Hess[12] in which a still is built in sections and has heating plates inclined alternately to right and left over which the crude oil flows, counterflow of vapours being prevented by a liquid seal.

The use of molten metal as a heating medium for oil has been the subject of many previous patents, but F. I. du Pont[13] describes a still in which the temperature of the molten metal is maintained by circulating a portion of it through an exterior heated system of pipes.

Improved efficiency in heat transfer is naturally a subject of interest to petroleum engineers, and M. Rowe[14] has patented a still composed of three concentric chambers in which the oil to be distilled passes through the exterior one, while hot flue gases enter the centre chamber, means being provided for separating the petroleum vapours from the flue gases.

A refinery on wheels has probably flitted before the imagination of more than one operator in regions where numerous small producing wells are remote from pipe-line facilities. That such a device is no mere "pipe-dream," is evidenced by a patent taken out by F. W. Sowell[15] for a portable refinery comprising a still, heat exchanger and cooling tower.

As regards fractionating devices mention may be made of the so-called "bubble tower" which although well known in Europe in

[9] U.S.P. 1,586,133.
[10] U.S.P. 1,587,370.
[11] U.S.P. 1,597,375.
[12] U.S.P. 1,608,741.
[13] U.S.P. 1,609,349.
[14] U.S.P. 1,610,594.
[15] U.S.P. 1,609,667.

several forms appears to have attracted attention in the United States only recently, and chiefly as an adjunct to cracking plants. It is computed that its use has enabled some refiners to increase the yield of straight-run gasoline from crude by from 6 to 8 per cent. Apart from this it appears to perform a special function with cracked spirit, the repeated washing of vapours by liquid oil being productive of polymerisation among the unsaturated and sulphur compounds present.

It is even claimed that with very sulphurous oils a definite saving in subsequent acid treatment and rerunning is brought about by its use, as compared with the ordinary dephlegmator.

Mechanical mixing devices for replacing air agitation continue to attract attention, although usually applied only to light distillates.

The usual arrangement comprises a centrifugal pump which circulates the oil and acid. The Marland Company in the United States are said to be using a mixer in which 4 four-bladed propellers revolve in a horizontal position within 3 eight foot lengths of standard 24-inch pipe. The propellers are opposed in direction in pairs, and rotate at about 100 to 150 R.P.M. The mixture of light distillate and chemical reagent is forced through the sections in turn by means of compressed air, and finally arrives at an agitator where the acid or other reagent is separated and pumped back to the first section, continuous circulation being maintained as long as necessary.

Before leaving the matter of refinery equipment mention should be made of the very serious attention given recently to the problems of corrosion of stills, dephlegmators and condensing equipment due to acid and sulphur compounds in the crude oil.

Undoubtedly the sulphurous Panhandle crude was responsible, to some extent, for bringing the matter more prominently to the attention of investigators in the United States, but the problem was by no means a new one there, and refiners of Mexican crude oil have for long been faced with the heavy expense of repairing and maintaining their equipment due to this cause.

The American Petroleum Institute was requested by G. E. P. Bly of the Standard Oil Co. of California to appoint a special committee on corrosion, and a large number of special articles have appeared in the technical press from time to time, dealing with the subject.

In a paper read by W. Miller of the Marland Refinery Co. before the A.P.I. meeting at Tulsa last December reference is made especially to the use of gaseous ammonia in overcoming the corrosion caused when distilling Panhandle crude. According to this author about 10 lbs. of ammonia per 1000 barrels of crude charged to the stills, is required, about half of this being fed into the crude stream from a drum connected with the inlet line of the crude feed pump.

The rest of the ammonia is introduced into the base of the final tower of the distillation system.

In the condensing system ammonia is found to be too expensive so a dilute solution of sodium carbonate (25 lbs. per hour of a 1 to 3 per cent. solution) is introduced at a point where the temperature is insufficient to vaporise the water. An alternative to the latter method is to introduce a large quantity of water into the vapour stream, from 1½ to 2 gallons of water per gallon of condensed distillate being mentioned as the amount required.

G. W. R. Finney and H. W. Young[16] describe experiments with lime, soda, sodium silicate and potassium bichromate and find that 2 lbs. of the latter substance per 1000 lbs. of water formed a solution which inhibited corrosion in water jackets, cooling towers and condensers in a natural gas compression plant. They state that the potassium salt can be replaced by sodium chromate, which is equally effective and cheaper.

In so far as corrosion is due to hydrochloric acid liberated from magnesium chloride in the water accompanying the crude, it would seem that the problem could be solved by previously removing this water.

The practice of the Amarillo Refining Co. is to divert the stream from the heat exchangers when a temperature of from 200° to 250° F. has been reached, the oil being passed into a closed settling tank provided with an outlet for the removal of any vapours evolved, which are returned to the distillation system, the salt water being drawn off from the tank.

Another system sometimes employed is to pass the oil through a washing system, the oil entering a tank through a distributing spider arranged on the bottom, and passing upwards through a layer of warm water, being finally drawn off as a supernatant layer from the top of the tank.

An article by H. Schmidt[17] deals with the question of corrosion and states that no satisfactory alloy has been found which could be used in practice to resist the action of hydrogen sulphide and hydrochloric acid. The best results were found to be given by nichrome, rustless steel and block tin.

When the oil and the water which accompanies it tend to form inseparable emulsions the use of aqueous solutions of neutralising reagents is prohibited, and the breaking of such emulsions is often a serious problem for the refiner.

R. A. Halloran[18] has patented the application of the acid tar obtained from kerosine sludge acid for this purpose. About 0·5

[16] *Oil and Gas J.* **25**, 33, 170.
[17] *Petroleum*, 1926, **30**, 1139-1140.
[18] U.S.P. 1,597,461.

per cent. by volume is used and the mixture with the crude oil is heated to 80° F.

Treating Methods.—Adsorption methods utilising Fuller's earth or some other form of clay continue to gain ground amongst modern refining methods, and a large number of specially prepared earths for this purpose have appeared on the market.

According to P. Truesdell[19] filtration of lubricating oils by the percolation method was prohibitive in California owing to the expense of shipping the earth from Georgia or Florida to the Pacific Coast. The contact method of filtration was the outcome of a search for a cheaper method. It is stated that a new form of roasting furnace for granular Fuller's earth has been invented which allows the refiner to regenerate his earth 25 to 30 times, thus bringing the percolation method again within economic limits and giving it a new lease of life.

On the other hand M. R. Mandelbaum and P. S. Nisson[20] have pointed out that Fuller's earth when used by percolation becomes less efficient with each revivification by burning but when used for vapour phase refining its value is undiminished.

H. Reinbold[21] claims a composition with bleaching and desulphurising properties which may be prepared by treating a hydrous aluminosilicate such as Bentonite with dry caustic soda, mixing about 25 to 40 per cent. of the latter with the earth and after reaction is complete, treating the mixture with chlorine. The product is said to be an intimate mixture of colloidal hydrous sodium aluminosilicate and sodium hypochlorite.

A preparation of the same properties is claimed by H. L. Kauffman[22] who treats finely divided Leverrierite for 7 hours at a temperature of 93° with 20 per cent. of sulphuric acid and washes the product with water.

As regards vapour-phase refining The Burma Oil Co. and R. R. le G. Worsley[23] have patented a method for employing Fuller's earth or other hydrosilicate, in which the latter acts on the fractions derived from petroleum, shale or paraffin wax in the vapour stage and under reduced pressure. It is stated that the temperature should not be greater than that necessary to maintain the oil in the vapour state, and that as high a vacuum as possible should be employed. These authors also claim that by mixing inert gases with the oil vapours the time of operation is reduced.

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[19] *Nat. Pet. News* **19**, 94.
[20] *Ind. Eng. Chem.*, 1926, **18**, 564-566.
[21] U.S.P. 1,600,845.
[22] U.S.P. 1,579,326.
[23] E.P. 260,455.

The problem of economically desulphurising petroleum oil products is perpetually confronting the refiner, and the year under review has produced still more contributions towards its solution.

M. Benton[24] mixes the oil with superheated steam and allows the mixture to expand. The hydrocarbons are fractionally precipitated with water and fractionation increased by spraying the vapours with the hydrocarbon condensate.

In the case of unsaturated and waste oil products J. A. Bishop[25] proposes to maintain the oil at from 450 to 500° F. while carbon monoxide and steam are introduced into the treating vessel independently. Carbon dioxide and nascent hydrogen are stated to be produced and hydrogenation takes place with the formation of hydrogen sulphide.

A somewhat similar principle is contained in the method of C. D. Maze[26] in which a mixture of steam and atomised oil is projected on to a heated catalyst. The formation of nascent hydrogen is stated to lead to hydrogenation and desulphurisation. The ratio of steam to hydrocarbon is 2:1, and the catalyst may be regenerated by increasing the proportion of steam in the mixture.

E. M. Johansen[27] has obtained a patent for a process in which an oil containing combined sulphur is mixed with one containing free sulphur, the mixture being then treated with alkaline plumbite solution.

Methods of solvent extraction as opposed to distillation have frequently been suggested, but so far have not found much favour in practice. The use of alcohol for this purpose is the basis of a method proposed by E. C. R. Marks[28] who treats topped oil with alcohol at a temperature of from 65° to 80° F. in successive stages, the solvent being recovered by distillation and dehydration. It is claimed for this method that the yield of desired product is 2½ times as much as that given by overhead distillation.

Although not a solvent extraction method it may be mentioned that the avoidance of distillation when seeking to obtain a product from crude oil was attempted by G. C. Davison of the Tri State Refining Co., Kenova, who dewaxed crude oil by diluting with naphtha, chilled the mixture and obtained the wax by centrifuging or cold settling.

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[24] U.S.P. 1,607,043.
[25] U.S.P. 1,610,242.
[26] E.P. 263,381.
[27] U.S.P. 1,587,649.
[28] E.P. 254,784.

Recovery methods.—The recovery of by-products resulting from refinery operations represents a field of wide scope for investigation, but has so far been little exploited. P. I. Schestakov[29] proposes to obtain sulphonic acids or their salts from oil by treating the latter with sulphuric acid, separating the acid tar, and heating the oil, if necessary, under pressure, to about 100° C. with acetic acid or one of its esters. The sulphonic acids are then said to be precipitated.

Alkaline sulphonates are said to be obtainable by similar treatment of the tar resulting from alkaline treatment of the oil.

The recovery of resinous substances from cracked distillates should be interesting if a practical application for such material was known. J. C. Morell[30] anticipates the latter contingency and has patented a method whereby the cracked oil is distilled with or filtered through an adsorbent material such as Bentonite or charcoal, the latter being then extracted with a suitable solvent such as ether, alcohol or liquid sulphur dioxide.

The recovery of sulphur from gases containing hydrogen sulphide is described by F. Fischer and P. Dithey[31], a solution of copper chloride in brine being used at a slightly elevated temperature, to scrub the gas. A yellow crust of almost pure sulphur is said to be formed, while the cuprous chloride produced is regenerated by blowing air through the solution.

Fire Fighting.—It has become customary to consider that by equipping tanks with foam distributing devices, the fire risk can be reduced to very small dimensions, and it is undoubtedly the case that in demonstrations made on a full-sized scale it has been shown that a burning tank can be extinguished very quickly. As in many other safety devices of this kind, it is the unexpected event which serves a useful purpose in demonstrating the fallibility of preconceived theories and leads to improvements in design. Early in January of last year a large storage tank half full of engine distillate at El Segundo Refinery, Los Angeles, caught fire and could not be extinguished in spite of the fact that it was equipped with a first-class foam system. The tank had a gas-tight steel roof and was being gauged at the time. It exploded and blew the roof off, killing the gauger. The foam distributors were not attached to the roof, the possibility of an explosion carrying them away having been foreseen, but the roof, after the explosion, fell back on the foam boxes, putting all but one of them out of commission. This one was put into use until a layer of foam 6 ft. thick had been formed in the tank, but the fire was not extinguished.

[29] E.P. 247,940.
[30] U.S.P. 1,608,135.
[31] *Brennstoff-Chem.*, 1926, 7, 300.

Subsequent investigation demonstrated that the efficiency of foam dropping from a height, as in a half-empty tank, is very seriously diminished, and experiments were carried out by using a number of portable extinguishers, which delivered the foam close to the surface of the burning oil through fireproof hoses. The latter method gave very encouraging results, and is commended to the notice of those readers who may be inclined to have too implicit faith in their foam system.

This possibility of explosion in the case of a partly filled tank seems to make a clear case for the floating roof as a better type of safety device, while for the purpose of diminishing evaporation losses through the "breathing" of tanks it is in several ways superior to the gas-tight roof with vacuum and pressure valves.

Miscellaneous.—The manufacture of asphalt is becoming of growing importance as the building of new roads and the maintenance of old ones keeps pace with the increasing use of motor vehicles. Several refiners now make specification asphalt in tubular stills, a possibility little thought of a few years ago. Blown asphalt also is in good demand, and methods for hastening the operating time are still generally unavailable. J. S. Miller[32] has patented a method in which the tar is heated and sprayed into a chamber, where it is brought into contact with gaseous oxidising and condensing agents.

The purification of asphaltic residues is the subject of a patent granted to S. W. Moss,[33] who describes a method of heating the material to the distilling temperatures in two stages, centrifuging it between each so as to throw out impurities.

The action of electric radiations upon oils is the subject of a paper by H. Becker,[34] which deals with the increase in viscosity in the case of mineral or fatty oils when subjected to the silent electric discharge. It is stated that the effect is accompanied by the evolution of hydrogen, and that the method is capable of application as a means of preparing that gas in a state of exceptional purity.

The electric discharge is also applied by D. L. Thomas,[35] who subjects cracked oils to a high tension silent electric discharge under high pressure, and claims that unsaturated compounds are polymerised with the production of stable products of different gravity and boiling point from those originally possessed by them.

A process invented by H. H. Reinbold[36] comprises the treatment

[32] U.S.P. 1,586,376.
[33] U.S.P. 1,599,369.
[34] *Wiss. Verof Siemens-konz.*, 1926, **5**, 140-166.
[35] U.S.P. 1,585,573.
[36] U.S.P. 1,570,005.

of oil with hydrated silicic acid in combination with a metal chloride, the oil being thereby bleached, cracked and desulphurised.

In a paper by L. Gurwitsch[37] some interesting observations are made regarding the regeneration of bleaching earth, and a new method is described for doing this without removing the earth from the filters. Briefly described, the method consists in extracting the earth with a mixture of benzene and alcohol, and then heating to about 150° C. The extracting power of the solvent is stated to depend upon the "heat of wetting." Alcohol has a high H.O.W. (17·2 calories) with Florida earth, but is not a good solvent. Benzene has a low H.O.W but is a good solvent; consequently a combination of the two is satisfactory. It is stated that Floridin was used for thirty successive operations after regeneration by this method without any marked diminution of its decolourising power.

Aluminium naphthenate is suggested as an addition to lubricating oils to increase their adhesive power for wet or dry surfaces and give them properties similar to those of castor oil, the author of this proposal being L. L. Rebben,[38] while de R. Frizell[39] claims that by adding up to 10 per cent. of sodium naphthenate to an oil the viscosity and stability are increased. This inventor also states that the addition of less than 1 per cent. of water to aluminium naphthenate increases its solubility in mineral oil.

Improving the quality of lubricating oils is also the subject of a patent granted to G. G. Acheson,[40] who extracts the oil with a mixed solvent such as an equal weight of 50 per cent. aqueous acetone, and claims that about 80 per cent. of an oil with a higher lubricating value than the original is undissolved by the solvent mixture and can be separated.

A method for continuously treating natural gasoline has been patented by Oberfell, Ballard, Alden, Usinger and Lentz,[41] who dissolve elementary sulphur in the gasoline and then pass the solution through a solution of caustic soda in water.

An interesting contribution to the literature of colloidal chemistry as applied to petroleum is that of P. J. de Kadt,[42] who describes experiments made with the object of converting asphaltic crude oil emulsions of the water-in-oil type into the oil-in-water phase, the latter being suitable for road dressing and roofing purposes. The inversion is brought about by the addition of rosin soap and distillation. Generally from 1 to 1·5 per cent. of rosin soap is

[37] *Kolloid. Zeit.*, 1926, **38**, 247-248.
[38] U.S.P. 1,582,227.
[39] U.S.P. 1,582,258.
[40] U.S.P. 1,548,588.
[41] U.S.P. 1,574,507.
[42] *Journ. Inst. Petr. Techn.*, 1926, **12**, 217-220.

added, and distillation proceeded with, sodium oleate is then added to the residue.

Amongst what may be termed patent curiosities for the year under review is that of G. E. High,[42] who proposes to carry on the distillation of oil or tar in the tanks of tank steamers during transit!

[42] E.P. 253,436.

American Refinery Technology.*

By Benjamin T. Brooks, Ph.D., F.C.S. (Member).

The American petroleum industry enjoyed a prosperous year in 1926. There have been no very novel nor outstanding developments, although gasoline cracking processes were much improved in the matter of daily throughput and gasoline production per unit; bubble tower distilling equipment has been more widely installed; radiant heat methods of heating have proven a success for heating the tubes of Cross cracking units; old-fashioned acid recovery plants have been replaced in many plants by the vacuum concentration method and the recovery system of the Chemical Construction Company; the high vacuum method of distilling lubricating oils has been improved as compared with batch distillation from shell stills by adopting the continuous pipe still system; natural gas gasoline recovery plants have been installed widely in new producing fields, but the recovery methods are substantially unchanged; the Gray method of refining cracked gasoline has been extended to a number of new installations; the distribution and sale of "Ethyl Gas" has been widely extended, and great interest continues to be shown in the anti-knock value of cracked gasolines; vapour phase gasoline has as yet found no substantial production; the paramount question in regard to gasoline refining appears to be the removal of sulphur, particularly from cracked gasolines made from high sulphur stocks.

The accompanying illustration (Fig. 1) shows one of the latest pipe still-bubble tower installations designed to take 90 per cent. distillate from Mid-Continent crude at a capacity of 5000 barrels per day, or when taking 50 per cent. overhead with a daily throughput of 9000–10,000 barrels per day.[1] The following results were

* Paper received May 25th, 1927.

[1] Primrose, *Oil and Gas J.*, Dec. 2, 1926.

obtained when operating at the higher capacity on Amarillo crude :—

Amarillo Crude.

Tube Still.

Inlet 350°.
Outlet 550°.
Throughput 9000–10,000 barrels.
Fuel 1·4 to 1·5 per cent throughput.

Tower.

Navy gasoline over top
Outlet temp. 305°.
Gravity 59·2°.
Initial 120°.
90 per cent. 392°.
End point 430°.

Kerosine
Gravity 41° to 41·5°.
Initial 410°.
End point 520°.
Flash 200°

Gas Oil
Gravity 35°–36°.
Initial 540° to 560°.
50 per cent. 630°

Bottoms
Gravity 27°.
Initial 560°–580°.
Flash 340° to 350°.
Loss 1 per cent.

Export gasoline over top
Outlet temp. 265°.
Gravity 63·0°.
Initial 105°.
90 per cent. 330°.
End point 375°.

Navy Naphtha
Gravity 47·5°.
Initial 340°–90 per cent. 395°.
End point 420°.

Gas Oil and Kerosine
Gravity 38·5°.
Initial 440° to 460°.

Bottoms
Gravity 27°.
Initial 560° to 580°.
Flash 340° to 350°.

Considerable flexibility in operation was obtained largely by varying the quantity of the reflux cooling medium while on stream, as shown by the following results :—

Method No. 1.

Overhead Gasoline—
Gravity 57·7° A.P.I.
Initial 119° F.
90 per cent.–412° F.
End point 438° F.

Fuel Residuum—
Gravity 29·5° A.P.I.
Flash 290° F.
Initial 510° F.
Throughput 7000 barrels.
Tube Still outlet 540° F.

Method No. 2.

Overhead Gasoline—
Gravity 59·8° A.P.I.
Initial 114° F.
90% 408° F.
End point 428° F.

Kerosine and Gas Oil—
Gravity 38·9° A.P.I.
Flash 295° F.
Initial 516° F.

Fuel Oil—
Gravity 27·0° A.P.I.
Flash 325° F.
Initial 548° F.
Throughput 8000 barrels.
Tube Still outlet 555° F.

Method No. 3.	*Method No.* 4.
Overhead Gasoline—	Overhead Gasoline—
Gravity 59·0° A.P.I.	Gravity 62·4° A.P.I.
Initial 118° F.	Initial 118° F.
90%–390° F.	90 per cent.–326° F.
End point 426° F.	End point 340° F.
Kerosine—	Naphtha—
Gravity 40·4° A.P.I.	Gravity 44·7° A.P.I.
Flash 200° F.	Initial 368° F.
Initial 424° F.	50 per cent.–402° F.
End point 542°.	90 per cent.–426° F.
Gas Oil—	End point 440° F.
Gravity 35·8° A.P.I.	Kerosine and Gas Oil—
Flash 310° F.	Gravity 37·2° A.P.I.
Initial 552° F.	Flash 300° F.
Fuel—	Initial 540° F.
Gravity 26° A.P.I.	Fuel—
Flash 340° F.	Gravity 26·8° A.P.I.
Initial 565° F.	Flash 340° F.
Throughput 10,000 barrels.	Initial 562° F.
Tube Still outlet 550° F.	Throughput 9200 barrels.
	Tube Still outlet 550° F

The second illustration shows the adaptation of bubble towers to a continuously operated battery of shell stills. In new installations the continuous pipe still-bubble tower type of equipment appears to be generally preferred, but the operation of existing shell still equipment in old plants is being greatly improved, in many plants, by equipment such as is shown in Figs. 2 and 3. A very common type of tower is shown in the background in Fig. 3.

In gasoline cracking plants making end-point gasoline, by the use of suitable bubble towers, the installation of the Gray Fullers earth process of refining has found favour. The Gray process has also been installed in a number of plants for testing pressure distillate, as it is re-run. The accompanying illustration (Fig. 4) shows such an installation of Gray treating equipment in the plant of the Marland Refining Company.

The ideal arrangement for the Gray process is one permitting the treatment of the cracked gasoline, of the proper end-point, as it is produced, thus eliminating re-running. The high boiling polymers, apparently formed from di-olefins, amount to about 0·5 to 0·8 per cent. of the gasoline treated. Sweetening is carried out in a subsequent operation. A standard size of apparatus contains 15 tons of Fullers earth and has a daily treating capacity of about 1200 barrels. The refining capacity varies considerably with the nature of the cracked gasoline and source of the Fullers earth, varying from about 1000 to 5000 barrels per ton of earth. Sixty refining units of the Gray process have been installed during 1925 and 1926.

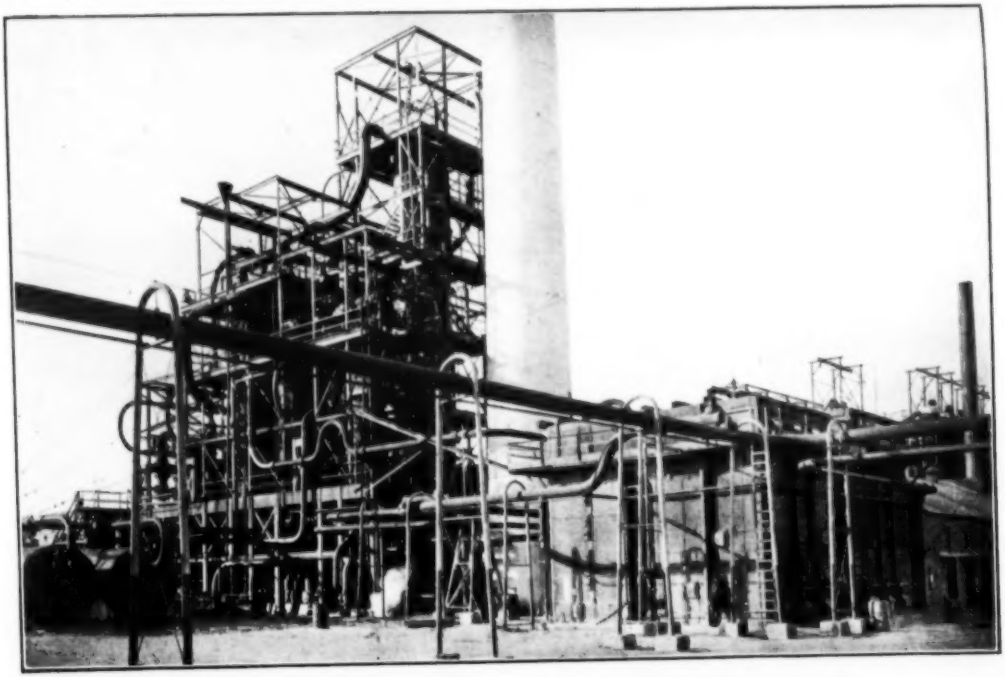

FIG. 1.

PIPE STILL AND BUBBLE TOWER INSTALLATION COMPLETED IN 1926 IN A MID-CONTINENT REFINERY.

[Courtesy of the Power Specialty Co.]

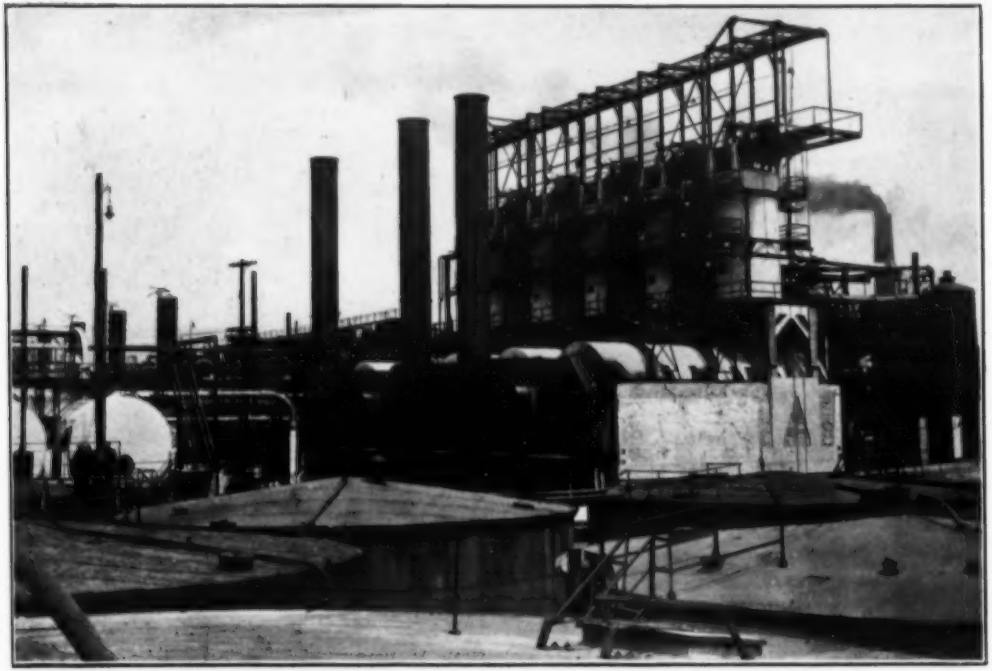

FIG. 2.

BUBBLE TOWERS ADAPTED TO A BATTERY OF FIVE SHELL-STILLS.

[Courtesy of E. B. Badger & Sons.]

BUBBLE TOWERS ADAPTED TO A BATTERY OF FIVE SHELL-STILLS.
[*Courtesy of E. B. Badger & Sons.*]

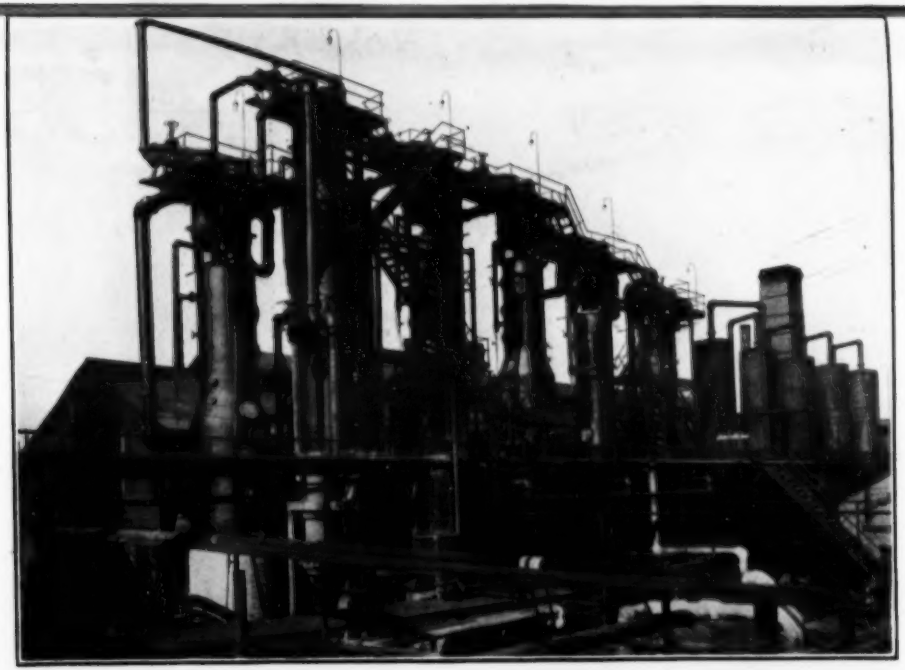

FIG. 3.

BUBBLE TOWERS ADAPTED TO A BATTERY OF OLD TYPE SHELL-STILLS, OLD TYPE OF TOWERS SHOWN IN BACKGROUND.

[*Courtesy of E. B. Badger & Sons.*]

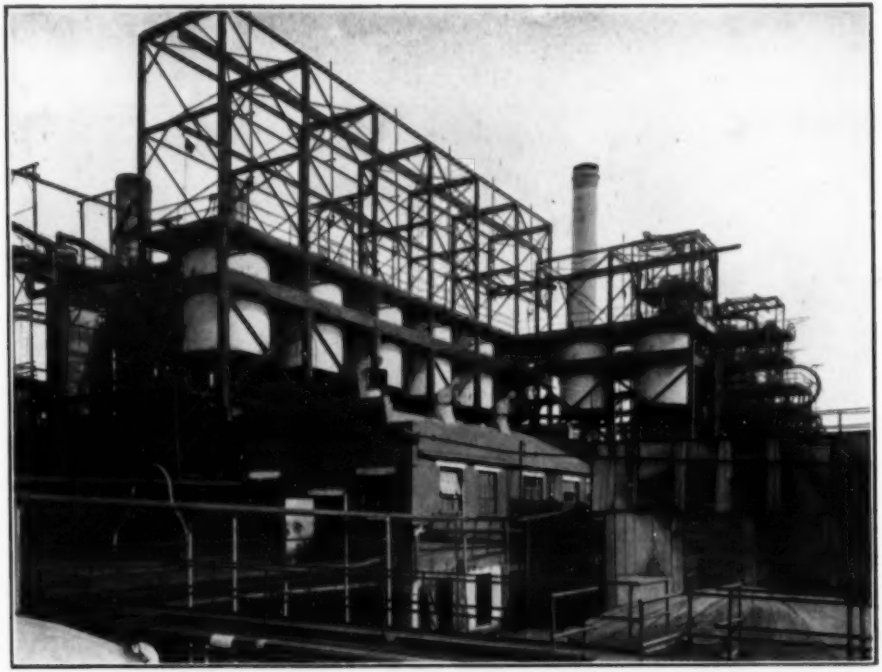

FIG. 4.

A RECENT INSTALLATION OF EQUIPMENT FOR REFINING CRACKED GASOLINE IN THE VAPOUR PHASE BY MEANS OF FULLER'S EARTH.

FIG. 4.

A RECENT INSTALLATION OF EQUIPMENT FOR REFINING CRACKED GASOLINE IN THE VAPOUR PHASE BY MEANS OF FULLER'S EARTH.

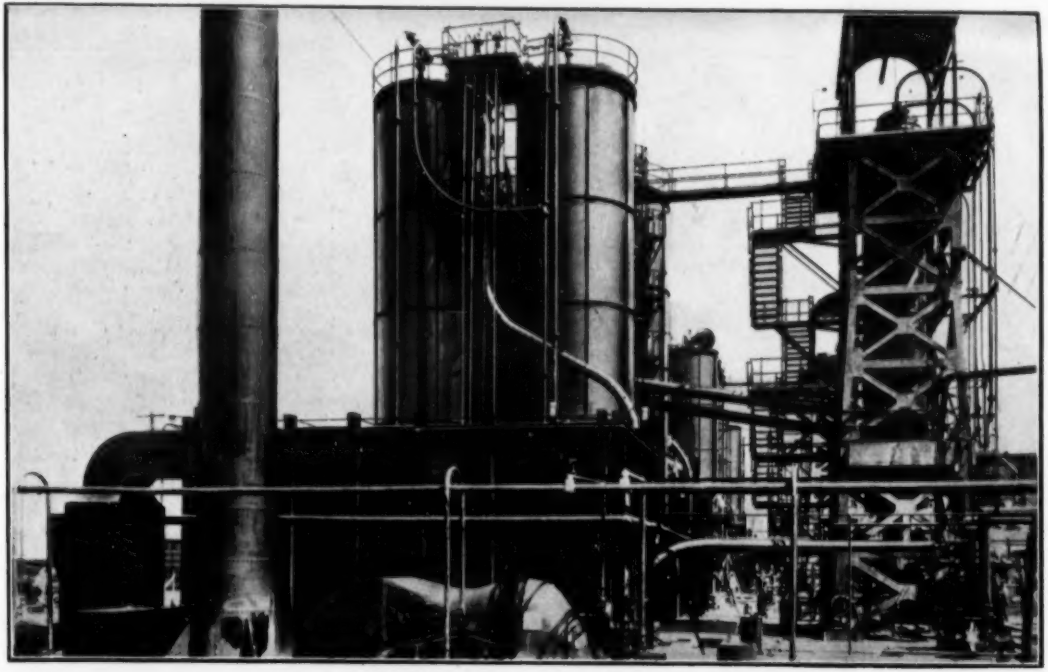

FIG. 5.

RECENT INSTALLATION OF DUBB'S CRACKING PROCESS SHOWING 10 X 40 FT. REACTION CHAMBERS.

[Courtesy of the Mineral Oil Products Co.]

The Holmes-Manly cracking process has increased the daily capacity of the standard unit from 1000–1200 barrels to about 2000 barrels per calendar day, not by increasing the size of the unit, but by improved methods of operation. The Holmes-Manly unit includes a large bubble tower operating under the full pressure of the system, with the result that the yellow colouring matter is polymerised or condensed producing end-point gasoline of satisfactory colour. The hot residuum is released to atmospheric pressure, and with the aid of steam is allowed to distill, producing 80–85 per cent. overhead distillate, which is recharged as cracking stock, and 15–20 per cent. heavy residuum or tar.[2] One of the straws which shows the way the wind is blowing, as it were, in refinery operation is the increasing use of automatic recording and control devices. Continuous distillation with bubble tower fractionation has required such mechanical auxiliaries, and de Florez[2] has pointed out the advantages accruing from such control of oil temperatures in the Holmes-Manly cracking process. In the case of a cracking unit, after a period of 3 or 4 hours of maintaining the temperature practically at the desired point the whole operation becomes smoother. The rate of cracking reaction and distillation becomes more constant, the tower reflux becomes more constant, and the rate through the circulating system also becomes more constant both in temperature and quantity. The resulting effect is that the back pressure on the feed becomes practically constant, which in turn stabilises the rate of feed. Thus, although only one automatic control is used on the still, the whole operation is stabilised and requires practically no adjustment. It will be obvious that this effect tends to increase the yield and uniformity of the products, in addition to which a saving is effected in fuel and in the maintenance of the heating surfaces due to more uniform operating conditions. The benefit derived from the increase in yield and capacity, however, is by far most important.

Figure 5 shows one of the most recent installations of the Dubbs cracking process, one of the most conspicuous features of which is the large "reaction chambers," two for each unit 10 ft. by 40 ft. in size. Beginning several years ago with 10 ft. by 10 ft. reaction chambers, their size has been gradually increased to take care of the large amount of coke formed, particularly when operating on heavy oil by the so-called non-residuum method. This has lengthened the continuous operating period. The disposition of the large quantities of coke produced in this way continues to be something of a problem, since hard burned coking still coke

[1] See U.S.P. to J. W. Coast, 1,585,233.
[2] *Am. Inst. Min. and Met. Eng. Annual Review of Petr. Technology* for 1926.

is preferred for the manufacture of electrodes and for metallurgical purposes, and the manufacture of briquettes from cracking still coke has apparently not yet been satisfactorily accomplished. Some plants have arranged to burn the coke under the boilers, and when sufficiently dry, it can be successfully pulverised in an aero pulveriser and burned like powdered coal. However, with fuel oil at an average price of $1·50 to $1·75 per barrel the equivalent price of the coke is about $8·00 per ton, or more than the average refiner can get for cracking still coke. In the past year, however, it has been found that even when cracking very heavy fuel oils the amount of coke deposited in the reaction chambers can be greatly reduced without appreciably diminishing the gasoline yield, by keeping a minimum amount of residuum in the chamber. It is reported that one plant, operating on heavy California fuel oil, has in this way reduced the amount of coke formed from 40–50 lbs. to less than 5 lbs. per barrel. The operating cycle, under these conditions, is limited by the deposition of coke in the heating tubes. The more ready saleability and generally greater profit of selling fuel oil, as well as the more serious explosion hazard of the large chambers indicates that future installations will return to much smaller sized chambers. As in the operation of the Holmes-Manley process, some licensees of the Dubbs process are reported to flash-distill the hot heavy residuum by releasing it to atmospheric pressure to obtain a clean fuel oil or re-cycle stock.

The Cross cracking process has also approximately doubled the daily throughput per unit; units formerly rated at 1000 barrels raw oil throughput are now putting through about 2000 barrels and the larger units which formerly were operated at 2000–2500 barrels of charging stock per day are now being operated at 4000–4400 barrels per day, with only a slight reduction in the gasoline yield, *i.e.*, about 33 per cent. to 30 per cent. This has been accomplished by pumping more charging stock through with a little more fuel consumption. The daily production of gasoline per unit is thus about doubled, and the operating cost per barrel of charging stock greatly reduced. The use of radiant heat for a part of the heating has been installed in some of the Cross units and a very material reduction in the amount and hardness of the carbon deposited in the "gun barrel" reaction chamber is reported.

Radiant heating of the hottest tubes in pipe stills has also been adopted in some of the latest designs. In both instances more even heating with fewer tube replacements, and reduction of the air excess to about 20 per cent. is reported.

In the Schulze process of distilling lubricating oils under very high vacuum radiant heat has been employed for heating shell

stills but this type of equipment has been superseded by continuous pipe stills operating under the high vacuum characteristic of the Schulze process. The Ziely Process Co. installed a demonstration plant in the summer of 1926, distilling reduced crudes for lubricating distillates using a pipe still, operated under a vacuum. High vacuum appears to be particularly applicable to the manufacture of lubricating oils from crudes substantially free from wax.

The so-called contact filtration of lubricating oils with finely ground Fullers earth, or acid-treated minerals of the bentonite type, is increasing in favour. Although the process is not new, having been used in the cottonseed oil industry for many years, the use of acid treated bentonite (and similar hydrated silicates) has greatly improved the results. For the literature on contact filtration the bibliography compiled by C. K. Francis should be consulted.[4]

In a recent discussion of contact filtration Mr. Walter Miller of the Marland Refining Co. stated: "It is a fact that one of the principal advantages of the contacting method is the reduction of the time element due to the much greater rapidity with which the absorbing power of the capillary surfaces can be utilised. This in turn makes for less equipment and investment. There is no difference of opinion about the materially lower investment cost for the contacting system. On the operating side, however, the case does not seem to be so clear. The lack of any practical method of recovering the finely ground fullers earth for re-use necessitating the discarding of the earth after one using, is quite an expensive proceeding. This is not offset by the somewhat cheaper price of the average fine clay used for 'dry' contact bleaching and is accentuated in the case of the very expensive acid treated types. Incidentally, the increasing use of the multiple muffle hearth furnace for burning and regenerating the coarse fullers earth is materially decreasing the cost of percolation filtering. This has increased greatly the number of times which coarse fullers earth can be re-used, as pointed out by H. W. Camp in a paper presented at the Western Petroleum Refiners' Association meeting at Wichita Falls in January of this year."

The crude so-called amorphous wax, often erroneously called "petrolatum" separated by the centrifugal process has heretofore been a waste product but a tough ceresin-like wax melting at about 74° C. has recently appeared on the market and is apparently manufactured from the undistilled wax separated in crude form by

[4] *Oil and Gas J.*, June 3, 1926, p. 156.

the centrifugal process. The commercial wax is dull yellow in colour and in the melted condition shows strong green fluorescence probably due to the presence of a little heavy oil.

The removal of sulphur from gasoline, particularly cracked gasoline, made from high sulphur crudes, is a refining difficulty of the first magnitude with certain refiners. Egloff and Morrell[5] have called attention to the large proportion of sulphuric acid required to reduce the per cent. of sulphur in certain refined cracked gasolines to 0·1 per cent. required by present specifications. Thirty or more pounds of acid per barrel are required in the case of cracked gasolines made from several of the California and Mexican oils. These authors give the percentages of sulphur in the charging stocks, unrefined pressure distillates and refined gasolines when treating with six to ten pounds of sulphuric acid to produce refined gasoline satisfactory in all respects save the sulphur percentage. They also point out that the use of excessive proportions of sulphuric acid reduces the anti-knock value of such gasolines.

The corrosion of refinery equipment by sulphur and salt water or hydrochloric acid has been much discussed and the seriousness of the problem is generally recognised. However, beyond reducing the corrosion of condensers by the use of ammonia very little in the way of helpful innovations has been accomplished.

Two of the researches provided for by the Rockefeller and Universal Oil Products Co's. bequest have to do with the study of the chemistry of organic sulphur compounds.

The recovery of light gasoline from refinery gases and from natural gas has reached such proportions that it has been more than sufficient for ordinary blending requirements and during most of 1926 was marketed at prices substantially below that of U.S. motor gasoline. Unless well fractioned the losses in transit in the summer months are very large. In this connexion considerable interest has been aroused in the pending litigation between the Phillips Petroleum Co. and the Carbide and Chemicals Corporation relative to the alleged infringement by the Phillips Co. of patents having to do with the fractional distillation or "stabilising" of natural gas gasoline. The case is significant as being one of a type frequently in the courts, involving the special application to a particular industry of a process generally old, in various modifications, in other industries.[6]

One of the most significant indications of the growing importance of research and scientific engineering in the petroleum industry is

[5] *Am. Inst. Min. and Met. Eng Annual Rept. on Petr. Technology* for 1926.
[6] *Oil and Gas J.*, Sept. 3, 1925.

the appreciation shown by many of the largest companies in the form of well equipped laboratories. It may be noted also that the Petroleum Division of the American Chemical Society is now the second largest Division in the Society. Another most satisfactory sign of the times is the attitude of most companies to reasonable publicity of research and even technical improvements. To this our technical journals bear almost daily witness.

Refining in Europe.*

By H. I. Waterman, Ph.D. (Member) and J. N. J. Perquin.

In this review consideration has been given to proper petroleum products only, and therefore alcohol and other products serving as substitutes for petroleum products have been excluded. Neither has the treatment of crude oil emulsions been considered, as this is no longer of such high importance as a few years ago.

In 1926 it was again proved that petroleum refining should be considered as an entirely new branch of chemical engineering, as the demands to which the products, gasoline, lubricating oil, transformer oil, asphalt, etc., have to answer are not yet completely settled. A fixed opinion on this subject is not yet attained, but new ideas have developed, and with these the refining technicians have to reckon.

The study of the anti-knock problem has proved the importance of the presence of unsaturated and aromatic hydrocarbons. Whereas the opinion several years ago was that the unsaturated hydrocarbons lowered the quality of the gasoline, the opposite opinion has now been settled. J. Tausz[1] states that the olefines and diolefines do not cause the colouring and sediment formation of the different species of gasolines, but is of the opinion that the chief cause of these deterrent properties is unsaturated hydrocarbons of a cyclic character, to which also belong unsaturated five-ring hydrocarbons. It is known that olefines may be oxidised, but the oxidation itself does not cause the colouring. Only in combination, with amines for instance, there may be formation of a dark colour. In this connection, the determination of unsaturated and aromatic hydrocarbons in gasoline is important, and

* Paper received May 18, 1927.

[1] *Z. angew. Chem.*, 1926, **39**, 685.

J. S. S. Brame,[2] in a discussion on the action of sulphuric acid of different concentrations on some hydrocarbons, has given a summary on the determination of these compounds. The halogen addition of the hydrocarbons was also considered, and W. R. Ormandy and E. C. Craven discuss their experiments on the action of sulphuric acid on gasoline. These investigators also studied the influence of a change in the concentration of the sulphuric acid used. They found that the specific weight and the refractive indices increase until the strength of the acid has reached about 88 per cent., which they explain to be caused by polymerisation and removal of unsaturated hydrocarbons. At higher acid strengths the aromatics are removed, and the specific gravity and the refraction are lowered. The concentration of 88 per cent. seems to be the critical point where the extraction of the unsaturated hydrocarbons is complete and the extraction of the aromatics just beginning. The large increase in acid loss which occurs if the acid strength exceeds 100 per cent. seems to prove that the free SO_3 has a very marked influence.

German investigators have, however, obtained results which do not agree with those obtained in England. E. H. Riesenfeld and G. Bandte[3] also studied the method of determination of unsaturated and aromatic hydrocarbons in gasolines, and their experiments led to their publishing the following methods of testing :—

1. Gasolines containing less than 5 per cent. by volume of unsaturated hydrocarbons are treated with sulphuric acid of 94 per cent. (2 parts acid to 1 part gasoline), being cooled with ice. The decrease in volume gives the percentage of unsaturated hydrocarbons. A second experiment is carried out at 40-45° C. with sulphuric acid of 100 per cent. in the same proportions. The decrease in volume gives the combined content of unsaturated and aromatic hydrocarbons. From the difference of the two determinations the aromatic content may be calculated.

2. Mixtures of benzene with the gasolines mentioned above, with an aromatic content of between 20 and 50 per cent. by volume, are treated by the same method, with the exception that 92 per cent. acid is used in place of 94 per cent.

Mixtures having an aromatic content of over 50 per cent. by volume are first diluted with normal gasoline (Kahlbaum) in the proportions of 1 : 1, and the determinations then carried out.

The authors point out that their method only holds for most of the German commercial gasolines, the unsaturated percentage

[2] *Journ. Inst. Petr. Techn.*, 1926, **12**, (54), 48.
[3] *Erdöl und Teer*, 1926, **2**, 587.

of which is generally less than 5 per cent. by volume. Their work cannot yet be considered as of general application.

Investigations concerning the explosion limits of hydrocarbons are of importance. Under the general title of "Explosive Reactions in Gaseous Media,"[4] a large amount of research work in this connection is published as a treatise of explosive reactions in general and as applied to internal-combustion engines.

In connection with the anti-detonating influence of different substances, C. J. Sims and E. Mardless have studied the effect of various metal colloids on the detonation of a commercial gasoline (B.P.) in a Ricardo Type E.35 motor, in which the compression ratio could be varied between 3·8 to 8. The colloidal solutions of the metals were prepared by heating the solution of the carbonyl-ethyl compounds after the addition of some rubber as a protecting colloid. The solutions of Fe, Pb and Ni colloids have an anti-detonation action. Using $Fe(CO)_5$, only a small weight was necessary to enhance compression ratio before detonation occurred. It is therefore considered by the investigators that $Fe(CO)_5$ is the best anti-detonator at present known. They also studied the influence of substances which, when heated, easily give metal particles in an active or pyrophoric form; some of them, such as Cu-oleate, Co-oleate, Co-xylyl, Co-naphtyl, Hg-amyl and dinaphtyl, colloidal C, etc., had no influence.

E. Berl and Günther Werner[5] have studied the limits of combustion of inflammable gas- and vapour-air mixtures at high pressures. This research is also of importance for those technical processes which are carried out under high pressures (Haber, Claude, Bergius), as well as for explosions in internal-combustion engines. The limits of explosions for mixtures of air with gases and vapours, such as hydrogen, ethylene, methane, ether and benzene, were fixed. They worked at pressures up to 600 atmospheres, and in some cases fixed the limits of combustion at pressures lower than 1 atmosphere. The benzene-air curve is particularly of importance for combustion engines, and one gets the impression more and more that it is extremely important to study the properties of each of the hydrocarbons separately.

The same principles are of value for the testing of lubricating oils, and in this respect A. Spilker[6] has done research work in connection with the lubricating properties of special compounds. He has the definite opinion that normal paraffins, even those of

[4] *Trans. Faraday Soc.*, 1926, **22**.
[5] *Z. angew. Chem.*, 1927, **40**, 245.
[6] Considerations about the Composition and the Chemical Constitution of Substances with Lubricating Character and the Synthesis of these Compounds. *Z. angew. Chem.*, 1926, **39**, 686, 997.

very high molecular weight, and aromatic ring systems do not give lubricating properties. It is in concordance herewith that the viscosity of lubricating oils is lowered by the addition of solid paraffins, and on the reverse is lowered by the removal of this wax. He also drew attention to the satisfactory lubricating character of products of addition and of condensation of benzene homologues with unsaturated compounds. He gives a survey of the viscosity of some addition- and condensation-products of the benzene homologues. The number of methyl-groups in the aromatic rings strongly enhances the viscosity and, therefore, the methyl-groups seem to have analagous importance in connection with the viscosity, as they are related to the colour of the aniline dyes.

Experiments prove more and more the importance of the properties of lubricating and transformer oil constituents towards the air-oxygen. H. Moore and J. Barnett[7] point out the importance of the resistance towards oxidation. In many cases this property is of more importance than the so-called "oiliness." Oxidation appears to be influenced in an unfavourable way by the sulphur content. G. Baum[8] states that complete refining with sulphuric acid especially has a favourable influence. In treating with sulphuric acid it is chiefly those substances which cause the high sludging values ("Verteerungszahl") of the transformer oils which are removed. He requires the percentage of these substances, chiefly unsaturated hydrocarbons, to remain small, less than 5 per cent. In this connection he considers it a wrong method to refine without sulphuric acid or with insufficient acid, e.g., with bleaching earth. W. Allner[9] has studied the evaporation of mineral oils and its significance for the application of air filters impregnated with oil. He investigated the evaporative power of mineral lubricating oil. At ordinary temperature this evaporation is very small only, but at higher temperature it becomes important. The conditions for the formation of oil vapours and of oil dew are mentioned, and it is proved that under normal conditions oil-clouds or -drips will not be formed in the oil-impregnated air filters.

H. Schering and R. Vieweg[10] have carried out research work with regard to the lubrication of ball and sliding bearings. With the latter only the measuring of capacity gives satisfactory results. They have studied graphically the way to directly find, from the electrical capacity, the smallest relative oil-layer thickness in sliding bearings.

[7] Some Experiments on the Oxidation of Lubricating Oil. *J. Inst. Petr. Techn.*, 1926, **12**, 582.

[8] Facts about the Testing of Transformer and Turbine Oils. *Z. angew. Chem.*, 1926, **39**, 473.

[9] *Z. angew. Chem.*, 1926, **39**, 16.

[10] *Z. angew. Chem.*, 1926, **39**, 1110, 1601.

Important perspectives are introduced by experiments on the regeneration of used lubricating and insulating oils. This problem is discussed by R. A. Wischin,[11] who applied a treatment with floridin, which it is possible is already applied in practice.

The importance of the study of the properties of the different hydrocarbons, such as the isolation of the constituents of crude oil fractions, is proved by the various workers who deal with this subject—e.g., J. A. Carpenter.[12] The same author, in a second paper,[13] gives a survey of the composition of Burmah and other kerosines. H. I. Waterman and J. N. J. Perquin and H. I. Waterman and J. C. Jamin[14] have investigated the polymerisation of different hydrocarbons, and have proved that the moisture content of polymerising agents, such as floridin, strongly influences the processes occurring. H. Staudinger[15] gives a general treatise on the chemistry of high molecular organic compounds.

The study of asphalt attracts increasing attention, and a paper by Ph. de Kadt,[16] who prepared asphalt-emulsions by the addition of soap, may be mentioned. His method also includes the treatment of crude oil emulsions.

During 1926 a great deal of work was carried out on cracking and hydrogenation, and it may be concluded that the more simple the basis of these experiments, the more useful and valuable are the results obtained.

The number of cracking patents increases continually, but only a few find application. The Dubb's process is successfully used in Rumania, and in Baku, Russia, a process of Kvito appears to have been applied since 1915.[17] In England, the A. D. H. process (Auld-Dunstan-Herring) has been thoroughly studied on a semi-commercial scale.[18] In this the process is carried out in three stages. In the first zone the oil is heated to 20-25° below the so-called "optimum" temperature—i.e., the temperature at which, under the conditions of the process (duration of heating, velocity of the oil stream), the predetermined degree of decomposition occurs. In the second zone the oil is rapidly heated to 20° above the "optimum" temperature in a "thermolyser," which

[11] *Z. angew. Chem.*, 1926, **39**, 685.

[12] The Physical and Chemical Properties of Paraffin Wax, particularly in the Solid State. *J. Inst. Petr. Techn.*, 1926, **12**, (56), 288.

[13] The Composition of Petroleum (Kerosine and other) Fractions, with the Standardization of Miscibility and Optical Tests. *J. Inst. Petr. Techn.*, 1926, **12**, (58), 518.

[14] *J. Inst. Petr. Techn.*, 1926, **12**, (58), 506, 510.

[15] *Ber.*, 1926, **59**, (2), 3019.

[16] *J. Inst. Petr. Techn.*, 1926, **12**, (55), 217.

[17] A. Tregoubof, *Azerbaidj. Neft. Choz.*, 1926, r53, 51-58. *Chim. et Ind.*, 1927, 39D, 1771.

[18] *Ind. Eng. Chem.*, 1926, **18**, 803.

consists of a number of vertical tubes of small diameter in which the oil can be quickly and thoroughly heated without appreciable formation of carbon. The third zone is the reactor, a vessel of such proportions that the oil remains sufficiently long for the required degree of decomposition to be reached. This reactor is maintained at the optimum temperature by external heating.

In the Machonin process[19] (Fr. P. 584,288) the cracking takes place in an apparatus directly connected with an internal-combustion engine. It can be heated, e.g., by the exhaust gases from the engine, and in this way it is possible to use heavy oil as the motor fuel.

In a paper by Herbst on the cracking of paraffin wax under the influence of active carbon,[20] the peculiarity of cracking taking place without the formation of carbon is described. Compared with the results obtained by the authors of this review, H. I. Waterman and J. N. J. Perquin,[21] this is in no way extraordinary under the circumstances. At a temperature of 300-400° C. during 42 hours, Herbst obtained 38·2 per cent. to 220° and 18·4 per cent. at 220-300° (calculated on the raw material, paraffin wax). At a temperature of 450° after about 50 minutes, Waterman and Perquin obtained about 40 per cent. to 220° and about 18 per cent. at 220-300° (interpolated in Fig. 1 of the article referred to), and they did not obtain a noticeable quantity of carbon.

Comparing the duration of both series of experiments, 50 minutes to 2,520 minutes, and assuming that for 10° the velocity of reaction is doubled, the temperature at which Herbst carried out his experiments may be calculated. It is assumed that the addition of active carbon has no influence. The authors' cracking process took place with a velocity 2^5 to 2^6 times faster and, therefore, the temperature in the Herbst process might be 390-400°. In addition, Herbst gives no details as to the quality of his products.

Closely connected with cracking is the preparation of synthetic gasoline. Two competitive methods are met, the Bergius process applied to coal, and the process of Fischer, who uses CO and H_2 mixture in the presence of catalysts as a raw material. During 1926 both investigators have published papers giving technical particulars, as well as economic details, of the commercial application of their processes.[22]

A. Spilker and K. Zerbe have contributed to the knowledge of chemical changes during hydrogenation. The direct addition during Berginisation of hydrogen to aromatic compounds, such as anthracene, is so rapid and goes so far that Berginisation may be

[19] The Machonin Process. S. Lavroff, *Petroleum*, 1926, **22**, 378.
[20] *Z. angew. Chem.*, 1926, **39**, 194.
[21] *J. Inst. Petr. Techn.*, 1925, **11**, (48), 36.
[22] *Z. angew. Chem.*, 1926, **39**, 339.

considered as the easiest way to prepare hydrogenation products of anthracene. No catalysts are required and careful preparation of the anthracene in advance is not necessary. From this it may be concluded that such hydrogenations only occur at a definite temperature, dependent on the nature of the compounds and on the working pressure. At this temperature the molecular-building becomes looser. In this respect the views of Spilker and Zerbe are in close accordance with those of Kling and Florentin,[23] and do not differ materially from the views of Waterman and Perquin, who concluded that in Berginisation there is no saturation of the unsaturated hydrocarbons already present, but only a hydrogenation of the products of decomposition obtained in cracking. Spilker and Zerbe lay stress on the fact that, together with the hydrogenation of these products of decomposition, the hydrogenation of the original unsaturated hydrocarbons may occur also at the temperature at which their decomposition begins. The hydrogenation of these unsaturated hydrocarbons may be the chief reaction. It is possible to use appropriate catalysts in Berginisation, such as $AlCl_3$, in order to lower the temperature at which decomposition of naphthalene commences, and then products of decomposition of naphthalene, such as benzene and similar compounds, are not formed exclusively, but the highest percentage of the reaction-product consists of hydrogenated naphthalene.

Spilker and Zerbe believe that the naphthalene complex is already considerably decomposed at 460°, and therefore at that temperature hydrogen at high pressure gives an important hydrogenation of the naphthalene, and only a small quantity of decomposition products is formed. They state that at temperatures higher than 460° the decomposition of naphthalene increases continually, and then the hydrogenation of the naphthalene molecule recedes into the background. These investigators have succeeded in allowing the hydrogenation of anthracene to dominate, and in their experiments only a negligible percentage of the anthracene is decomposed. The small quantities of methane, in the gases formed during the reaction, and of naphthalene, in the reaction-products, must be put down to this decomposition.

In connection with Berginisation, Heyn[24] has carried out research work on the Berginisation of coal. He investigated the gasoline obtained from the Berginisation of Lower Silesia coals, and found different hydro-aromatic hydrocarbons, such as cyclohexane and methyl- and dimethyl-cyclohexane, tetra- and deca-hydronaphthalene.

[23] *Comptes rend.*, 1926, **182**, 389, 526.
[24] *Z. angew. Chem.*, 1926, **39**, 687.

The investigations of Franz Fischer, at Mülheim-Ruhr, on the synthesis of petroleum, although not directly connected with refining, are worthy of mention. During 1926 several articles on this subject appeared in the technical journals. The application of high pressure is not necessary in synthesis, and it has become possible to prepare pure aliphatic petroleum products in a simple manner. In Fischer's method mixtures of hydrogen and carbon monoxide, in varying proportions, are taken as the raw material and, with the aid of catalysts, this mixture is transformed at a low temperature. It is possible to use water-gas, but it is absolutely necessary to purify the gas and remove the sulphur compounds. The catalysts generally used contain iron or cobalt as active ingredients. At first the difficulty was to prevent the formation of CH_4, thus only preparing the higher boiling gasolines and even solid paraffins. With each catalyst the most suitable temperature must be chosen, but must usually remain below 300°, as at a higher temperature chiefly methane is formed. In this process we have a combination of hydrogenation and polymerisation. The average molecular weight of the hydrocarbons obtained by synthesis depends on the basicity of special ingredients added. The nature of the products formed may be varied therefore by, among others, substances with a gasoline character on one side and solid paraffin on the other. Fischer thinks that higher metal-carbides serve as an intermediary product.

In refining in general sulphuric acid and lye are still used. Lye is sometimes replaced, wholly or partially, by alkalic bleaching earths, and in Germany especially by the so-called Bavarian earth.[25]

The difficulties in using sulphuric acid are numerous, e.g., the strong polymerising, sulphonising and oxidising action. Sulphuric acid may also cause the formation of oil-soluble substances which are the cause of emulsion formation. In special cases difficulties arise, and there is a tendency to replace the sulphuric acid by other reagents or to limit the quantities used in refining. A means of refining used in an increasing number of refineries is the extraction with liquid SO_2, followed by a treatment with smaller quantities of acid. By this means a part of the oil is obtained as an extract which may be used for different purposes. The extract of kerosine may be used for mixing with gasoline to the advantage of its "anti-knock" properties.

Schwarz[26] gives a method to partly prevent the objections to refining with sulphuric acid. Under certain circumstances he adds soaps with an excess of alkali, and substances having emulsifying properties are precipitated as a viscous, thick, dark coloured liquid

[25] G. Schiller, *Petroleum*, 1926, **22**, 123. Löb, *Petroleum*, 1926, **22**, 171.
[26] *Petroleum*, 1926, **22**, 576.

mass. The quantity of this precipitate depends on the general circumstances of the experiments, and particularly on the soap-content; in preparing transformer oil from a Russian distillate with soap and alkali, 5 per cent. of a dark oil was precipitated. This refining with soap can be used as a preliminary refining, or as a single means of refining, and in the latter case only bleaching is required afterwards. In handling dark distillates, the soap is used as a preliminary refining agent, followed by acid treatment. The refining with acid is made easier, less acid is required, there is no formation of emulsions and the refined oil has a greater resistance against heating.

The precipitate obtained with soap may be used as a water-soluble oil. Schwarz also recommends the treatment with soap for the preliminary refining of crude oil, as in this case the distillation proceeds better, the oil being more resistant to heating and the crystallisation of paraffin wax is better.

A number of patents are found proposing different substances as refining agents, e.g., $SnCl_4$ and Fullers Earth (Hugo Stinnes Riebeck's Montan u. Olwerke A.G., D.R.P. 421,858), $HgSO_4$ (F. Remfry and A. E. Dunstan, E.P. 246,937), etc. The value of these substances for refining has still to be proved, and a favourable reaction on the oil must be combined with the possibility of regeneration of the refining agent.

Probably the general considerations on the action of different refining agents are more important than many technical experiments.

Otto Ruff and P. Mautner[27] discuss the active forms of silica acid (the silica gel) and its adsorptive power. In judging the adsorptive power they distinguish three actions:—

1. The adsorptive power for gases and for chemically indifferent substances in general. This power would be in connection with the development of the surface of the adsorbent, the substance with the most developed surface and the finest pores having the best adsorptive power.
2. The adsorptive power for molecular disperse solutions of chemically active substances.
3. The adsorptive power for colloidal substances.

Silica gel will have little activity in connection with 2, except in the desulphurisation of crude oil. The investigators think that there is a possibility in the latter case that it is not adsorption of molecular disperse substances, but of colloidal substances (3),

[27] *Z. angew. Chem.*, 1927, **40**, 428.

which have to be dealt with. Our knowledge of the composition and of the properties of different petroleum distillates is insufficient, as is also our knowledge of the refining agents now in use, and of their action on the constituents of the distillates.

Our knowledge of the chemical changes which occur in the thermal decomposition and hydrogenation processes is also small.

There is no wonder, therefore, that the writers of this review do not judge favourably on the results obtained in refining during 1926. It is only by the intense study of the lacking scientific knowledge that the rapid growth of the chemical technology of oil refining may be assured.

The Fractionation of Petroleum.*

By E. H. Leslie, Ph.D.,
Professor of Chemical Engineering, University of Michigan.

The year 1926 has witnessed rapid progress in the betterment of methods for distilling petroleum, particularly in the application of the principles of fractionation by counter-current extraction so well known and long applied in many other industries.

Broadly speaking, from a physical and engineering standpoint, the distillation of petroleum requires consideration of four major problems :—

1. The transfer of heat to the oil.
2. The manner of formation of the vapour.
3. The fractionation of the vapour to form the required products.
4. The recovery and removal of heat from the vapours, distillates and residual heavy oil.

This review is limited largely to the second and third points, with limited comment on the first.

The Transfer of Heat to Petroleum Oil.

The design of apparatus for transferring heat to petroleum oils requires knowledge of :—

(*a*) Combustion, radiation, and the mechanics of flow of furnace gases.

* Paper received May 14th, 1927.

(*b*) The mechanism and rate of the transfer of heat to a metal wall and from a metal wall to oil.

(*c*) The quantity of heat required to raise oils of given density and temperature 1° F.

(*d*) The quantity of heat required to form 1lb. of vapour of given composition.

Further than this, a decision must be reached as regards the type of equipment to be most advantageously used, that is, whether shell-stills or pipe-stills will best give the required result.

As regards the first point, one observes a tendency on the part of refiners to give reasonable attention to such elementary considerations as the use of efficient oil burners or stokers, the admission of a moderate excess of air only, the preheating of admitted air, and the use of economizer heat transferring surfaces to reduce the temperature of the outgoing flue gas. To an increasing degree, also, the importance of the transfer of heat by radiation is being realized. In shell-still practice this means larger radiating wall surfaces, and, in pipe-still practice, exposure of a large part of the heating surface, rather than a small part, to radiation from the combustion gases and walls of the combustion chamber.

Shell-stills are now frequently equipped with tubes through which the outgoing flue gas is caused to pass. Furnaces and still units of this character are now operating in several refineries with overall thermal efficiencies of 80 per cent. or slightly higher. This is a great improvement over efficiencies of 30 per cent. to 50 per cent. so common only a short time ago in most plants, and still the rule in many refineries.

Pipe-stills, in general, have operated at higher thermal efficiencies than shell-stills, but as usually constructed have been needlessly expensive because of the low rate of heat transfer in the economizer or convection section. In pipe-stills of the latest design the average or overall rate of heat transfer has been greatly increased by exposing almost the entire heating surface to radiation, thus absorbing the larger part of the available energy by radiation and leaving a small part only to be removed in the convection section in preheating oil or air for combustion. A further serious difficulty with many pipe-stills heretofore constructed has been unequal heat transfer rates at different parts of the heating surface, with the result that localized overheating of the metal tubes concerned, and, consequently, oxidative failure. In recent designs this has been eliminated.

The use of carborundum muffles, or combustion conduits made of similar refractory materials, has been widely advocated during

the past year. The advantage claimed is rapid combustion in the refractory muffle with uniform radiant transfer of heat from the exterior surface of the muffle. Critical consideration of the practical use of this procedure leads to the conclusion that good results can be secured if the overall rate of heat transfer through the metal surfaces to be heated need not be high. The inhere limitation of the combustion muffle is the thermal conductivity of the refractory. For structural reasons, the tiles or brick cannot be made too thin. Even as they are now constructed breakage is excessive. Hence, if high rates of heat transfer are required, better results will be had with a plain combustion chamber of ample size.

Some attention has been given recently to the placement o bridge walls and baffle walls beneath shell-stills and in similar surfaces. In most existent still settings the colder flue gas is caused to flow uphill, mixing with the hotter flue gas at a higher level, with the consequence that no opportunity is afforded for the normal stratification of the combustion gases as to temperature and density, and with the definite result of lowering the average temperature of the flue gas as a whole and raising of the temperature at which the gas leaves the setting. A few engineers have come to appreciate and apply the principles of furnace design outlined by Groume-Grjimailo,[1] and now eliminate all baffles and obstructions from still settings, thus permitting the normal stratification of the combustion gases, raising the setting wall temperature so that a larger wall area functions radiatively decreasing effluent gas temperature, and in general improving furnace operation and efficiency. This subject is worthy of much further thought.

The technical literature of the past year affords little of value on the subject of rates of heat transfer to oils. However, the industry is making a definite improvement along these lines. One refinery with an unusually competent technical staff has succeeded in operating shell-stills at an overall transfer rate of 25,000 to 30,000 B.Th.U. per hour per square foot of projected surface.[2] On this basis a single 12 ft. × 32 ft. still will handle over 6000 barrels of crude oil per day, vaporizing 50 per cent. Special provision for forced circulation of the oil inside the still is, of course, necessary.

Many shell-stills are operated at overall transfer rates of 15,000 to 17,000 B.Th.U. per hour per square foot projected area.

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[1] "The Flow of Gases in Furnaces." J. Wiley & Sons. Translated by A. D. Williams. 1923.

[2] Length × diameter = projected area.

On the other hand most are running at rates of 10,000 B.Th.U. on down to 4000 or 3000. Thus, some refineries are now using a whole battery of stills to do what a competitor does in a single still. Such contrasts as this clearly point to the need for more general technical service throughout the industry.

One of the most urgent needs of the industry from a technical standpoint is more accurate physical data, particularly data on specific and latent heats. This is apparent to any engineer who is regularly required to design equipment for heating and distillation. Progress in this direction has been made during 1926, although the results of this work are not yet wholly available in published form. Among the more important technical papers dealing with thermal data are those of E. H. Zeitfuchs,[3] A. R. Fortsch and W. C. Whitman,[4] and Leslie, Geniesse, Legatski and Jagrowski.[5]

Table I. presents a comparison of specific heat data for petroleum oils. The U.S. Bureau of Standards data are from a private communication to the writer. The equation is :—

$$C = \frac{1}{\sqrt{D}} \quad [0{\cdot}415 + 0{\cdot}00045\,(t-60)]$$

in which D = Sp. gr. 60° F./60° F.

The International Critical Table equation was one derived to represent the mean of the most reliable data existent at the time of preparing the manuscript for these tables. It is :—

$$C = \frac{A}{\sqrt{D^{15}/_{4}}} + B\,(t-15) \quad \text{in which}$$

A = 0·425 for paraffin-base oils.
0·405 for naphthene-base oils.
0·415 for mixed-base oils.
$10^3 B = 0{\cdot}90$ for all oils.

The Eckart data are from an article by this author.[6] The Standard Oil (Indiana) data are those of Fortsch and Whitman.

In the writer's opinion the U.S. Bureau of Standards data are the most reliable. It will be noted that they are in close agreement with those of the International Critical Tables and Standard Oil (Indiana). Eckart's values are clearly too high.

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[3] "Specific Heats, Heats of Vaporization and Critical Temps. of California Petroleum." *Ind. Eng. Chem.*, 1926, **18**, 79-82.

[4] "The Specific Heat of Oils." *Ind. Eng. Chem.*, 1926, **18**, 795-800.

[5] "Latent Heat Vaporisation of Dists. from Paraffin-Base Petroleum." *Ind. Eng. Chem.*, 1926, **18**, 45, 46.

[6] *Mech. Eng.*, 1925, **47**, 535-540.

The important influence of both density and temperature on the specific heat should be noted, and the common practice of using a value of about 0·5 for any and all cases abandoned.

TABLE I.

COMPARISON OF SPECIFIC HEAT DATA FOR PETROLEUM OILS.

Sp. gr. at 60/60 Temp. ° F.	U.S. Bur. Standards Equation.	Int. Crit. Equation.	Eckart.	S.O. Indiana.
0·64 at 100	0·543	0·540	0·554	—
0·64 at 400	0·710	0·689	0·847	—
0·64 at 700	0·878	0·839	—	—
0·70 at 100	0·517	0·518	0·535	—
0·70 at 400	0·678	0·667	0·820	—
0·70 at 700	0·841	0·817	—	—
0·80 at 100	0·485	0·485	0·500	0·494
0·80 at 400	0·635	0·634	0·766	0·684
0·80 at 700	0·787	0·784	1·033	—
0·92 at 100	0·450	0·454	0·460	0·445
0·92 at 400	0·592	0·603	0·705	0·620
0·92 at 700	0·734	0·753	0·952	—
1·00 at 100	0·433	0·436	0·435	0·418
1·00 at 400	0·568	0·585	0·667	0·580
1·00 at 700	0·705	0·735	0·896	—

Data on latent heats are fewer and less reliable. Table II. presents values that can be used tentatively until more accurate determinations have been made and published. They are taken from unpublished results secured in the writer's laboratory during the last two years, and agree fairly well with values calculated from the Hildebrand modification of Trouton's rule.

TABLE II.

LATENT HEATS OF VAPORIZATION OF PARAFFIN-BASE AND ASPHALT-BASE PETROLEUM HYDROCARBONS.

Temp. ° F.	Latent Heats per 1 atm. Pressure as B.Th.U. per lb. Paraffin-Base.	Asphalt-Base.
100	148	153
200	134·5	139
300	123	126·5
400	112	115·5
500	101·5	106
600	91·5	97·5
700	82	89

THE FORMATION OF VAPOUR FROM PETROLEUM.

The way in which vapour is formed from petroleum is a subject to which all too little attention has been directed in the past If a given per cent. of an oil is to be vaporized shall this be done by a single flash vaporization as from a pipe-still and vaporizer system, by multiple flashing using a series of pipe-stills, by use

of a series of shell-stills, by a single shell-still operated as a continuous unit, or by batch distillation from a shell still? What are the consequences and relative economies of these several procedures? Because the technical literature contained no adequate answer to such questions an investigation was started two years ago, the results of which have recently been published.[7]

On the one hand is the limiting process of differential vaporization that is approximated in practice by batch distillation. At the other extreme is incremental vaporization or the single equilibrium flash vaporization, approached in practice by the pipe-still and flash vaporizer. Between these two extremes are numerous procedures each typified by a definite result. For example, removal of vapours from each of several shell-stills, operated as a continuous battery with oil flow from still to still, can be designated as differential incremental vaporization.

As an example of the difference in result secured by distillation from a batch still as compared to a pipe-still flash, in each case operating at the same final temperature, 590° F., it can be stated that only 54 per cent. of a given oil was vaporized by the differential process, whereas 77 per cent. was vaporized by the equilibrium flash. The residuum from the differential process contained 2·4 per cent. (based on the crude) boiling below 450° F., whereas that from the equilibrium flash contained less than 0·1 per cent. To vaporize 54 per cent. of the crude by the equilibrium flash necessitates heating only to 445° F. However, the residue in this instance would contain 4·4 per cent. (based on the crude) of distillate boiling below 450° F. To strip the residue to a 2·4 per cent. content of distillate boiling below 450° F. would require an equilibrium flash at about 490° F. This is a 100° F. lower than the temperature required for a like exhaustion of the residue by batch distillation.

In the article by Leslie and Good, to which reference has been made, a comparison is made of equilibrium single flashing and equilibrium successive flashing at 50° F. temperature intervals from 250° F. to 600° F. Equilibrium single flashing was found superior to successive flashing as regards yield of distillate, exhaustion of residuum, composition of vapour, and heat requirement. The proportion of a single flash distillate boiling below the flash temperature averages 82·3 per cent. and of a successive flash distillate 80·65 per cent. The proportion of a single flash residuum boiling above the flash temperature averages 11·6 per cent. and of a

[7] E. H. Leslie and A. J. Good, "The Vaporization of Petroleum." *Ind. Eng. Chem.*, 1927, **19**, 453-460.

successive flash residuum 16·4 per cent. The A.S.T.M. endpoint of a single flash distillate is about 150° F. above the flash temperature, and of a successive flash distillate, 135-140° F. above the final flash temperature. In general, the data in the article will be found helpful in estimating the quantity and quality of the vapour and residuums formed by flashing a petroleum of approximately 50 per cent. 437° F. endpoint gasoline at different temperatures. Similar data are now being secured for typical pressure distillates and for crude oils containing approximately 20 per cent. and 36 per cent. gasoline. This work is being done under a fellowship grant of the American Petroleum Institute.

Such investigation of vaporization procedure as had been made to date indicates that this subject has been given too little consideration heretofore. The batch still is bad, not only for operating reasons, but inherently. Batteries of shell-stills possess inherent disadvantages as vapour formers as compared to the single flash pipe-still or single continuously operated shell-still. These should be recognized.

The Fractionation of Petroleum Vapours.

Other than the more general use of cracking processes no technological movement in the industry is of greater significance than the appreciation of the excellent results to be secured by applying the principles of effective fractionation. The year 1926 is the first of which it may be said that petroleum refiners in general have been alive to the advantages of column fractionation as distinguished from such fractionation as is secured by partial condensation of the vapour to be treated. However, there are still numerous operators and not a few technical men who do not clearly distinguish between partial condensation as a type process and fractionation by counter-current contracting in a column or "bubble-tower" as another type process. Results can be secured by the second that are not possible with the first.

One of the factors responsible for the general lack of knowledge regarding column distillation is the limited technical literature treating of the subject as a whole and the almost negligible number of papers dealing with the fractionation of petroleum specifically. The more important general papers are limited to a discussion, in somewhat formal mathematical language, of binary or ternary systems. Hence, although qualitatively applicable, such information as has been available in the technical literature can hardly be said to have been directly and quantitatively applicable to the design problems of the refinery engineer.

A few equipment organizations have secured the services of distillation specialists, and through correlation of the results of laboratory and plant investigations have determined a reasonably satisfactory basis for the design of petroleum fractionation equipment as regards diameter for a given capacity and plates required for effecting the required amount of fractionation. That such data are not in the hands of many designing engineers is evidenced by the clumsy and oversize equipment frequently built.

Illustrating the point that the building of fractionating columns is specialized work is the fact that columns are now constructed with plate efficiencies varying from 20 per cent. to 80 per cent. Furthermore one sees a 5-plate column doing a given job in one refinery and a 20-plate column doing the same work in another. Where knowledge is limited, practice will, of course, be diverse. The redeeming feature of all this is that almost any fractionating column is so much better than air-cooled or liquid-cooled fractionating condensers, that inexact design is pardonable if equipment is thereby secured and put to work sooner than would be possible otherwise

Viewing the year 1926 as a whole it can be said that it is characterized by the wider use of counter-current fractionating equipment in the industry as a whole, and by the more advantageous use of such equipment in special arrangements by those best versed in knowledge of the subject.

A few papers not dealing specifically with the distillation of petroleum but treating of the theory of fractionation have appeared during the past year.

L. Gay[8] discusses the problem of the complete separation of a solution of four or more components. A graphical method is developed for calculating the relationship between heat flow and the compositions of the vapour and liquid phases at any point in the two columns. The paper is a continuation of the previous excellent papers by this author covering binary and ternary systems.

T. S. Carswell[9] mathematically analyzes the relationship between the H.E.T.P.[10] and the properties of the liquid distilled and diameter of packing used in a filled column. The H.E.T.P.=47r in which "r" is the radius in cm. of the packing rings. For a given column

[8] *Chim. et Ind.*, 1926, **15**, 3-13, 173-183.

[9] "Fractionating Column Calculations." *Ind. Eng. Chem.*, 1926, **18**, 294, 295.

[10] See Peters, *Ind. Eng. Chem.*, 1922, **14**, 476.

and type of packing the height of the equivalent theoretical plate is given by the equation

$$H.E.T.P. = K\frac{Md}{T} \text{ — in which}$$

M = mol. wt. of the substance.
d = density of the backflow at the temperature of the distillation.
T = absolute temperature of distillation.

The article relates to packed columns, and is therefore of minor importance to the refinery engineer, who should realize that large diameter packed columns are of little practical value. It will be of interest, however, to the experimentalist who uses filled columns in laboratory or semi-works operations.

W. G. Whitman and G. H. B. Davis[11] compare the processes of gas absorption and rectification by absorbing carbon dioxide from a flue gas with a carbonate-bicarbonate lye, and on the other hand contacting a gas phase composed of steam and carbon dioxide with the same alkali. The overall absorption co-efficient was found to be proportional to the square root of the gas velocity through the column. The co-efficient for rectification was 2·4 times that for absorption. These points are of interest to petroleum technologists because of the recent highly successful application of bubbler cap columns as absorbers in natural gasoline recovery and in the treatment of refinery gases.

K. V. Kostrine and K. V. Michtchenko[12] studied the effect of steam on rectification in plant size equipment. They concluded that steam had a detrimental effect on rectification, because a given fraction secured by steam distillation showed a wider distillation range than the analogous dry distilled fraction. In the writer's opinion this result is open to confirmation.

A. Dobrjanski and K. Matussorski[13] report the results of laboratory experiments in which a topped petroleum was vaporized at 250° C. by passing various gases through it. Coal gas, air, carbon dioxide, and hydrogen were used. The time of distillation was proportioned to the square root of the density of the gas passed.

One of the factors most necessary to improvement of plant methods is a reliable yardstick with which to measure performance. Viewed in this light the development of precise laboratory distillation methods is of special interest and importance. In general it can be said that laboratory methods of fractionation have been inferior to those used in the plant. Most of the methods

[11] "A Comparison of Gas Absorption and Rectification." *Ind. Eng. Chem.*, 1926, **18**, 264-266.
[12] *Azerbaidj-Neft. Chos.*, 1925, No. 11, 71-79. See *Chim. et Ind.*, 1927, **16**, 69.
[13] *Neftjanoe Chozjajstro*, 1926, **10**, 236-242. *Chem. Zentr.*, 1926, II, 303.

used in the organic chemical laboratories are archaic. In view of the glass blowers' dreams that pose and have been used in many instances as fractionating devices the several articles appearing during the last year have special significance.

W. A. Peters, jr., and T. Baker[14] describe a precision substantially adiabatic fractionating column with which excellent analytical results have been secured. The column and condenser are designed so that the liquid hold-up is minimized. Heat is supplied electrically to the flask, airheater, and jacket wire heaters. This column and its application to the distillation of petroleum is also described by Peters and Leslie.[15]

E. H. Leslie and J. C. Geniesse[16] have investigated the performance of a nearly adiabatic vacuum jacketed laboratory column with regard to effect of vapour velocity, reflux ratio, size of packing, heat losses, and thermal efficiency. The results are of interest both in laboratory and plant work.

H. G. Vesper[17] describes the four point method used by the Standard Oil Company of California. Two distillations are involved, a preliminary topping followed by Hempel column distillation of the tops. The whole procedure is an empirical one. The first distillation is carried only to 600° F., assuming that no gasoline is left in the residue at this temperature, an assumption that is in error.

A. W. T. Loveless[18] describes a column similar to that of Leslie and Geniesse, suggesting that it is an improvement on that of Peters and Baker. However, the column is too large in diameter to be effective as an analytical instrument unless a large sample is distilled. A long small diameter column, such as that of Peters and Baker, is not only to be preferred, but is absolutely necessary if precise results are to be secured in reasonable time.

H. T. Clark and E. S. Rahrs[19] use a still-head that causes the vapour to bubble through the liquid. The objection to this device as an analytical column is the large weight of liquid in the column.

An interesting article reporting tests of the accuracy of the A.S.T.M. distillation method is published by the laboratory of the Bataafsche Petroleum Maatschappij.[20]

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[14] "High-Precision Fractional Distillation in the Laboratory." *Ind. Eng. Chem.*, 1926, **18**, 69-73.

[15] *The Oil Trade*, 1926, **17**, No. 3, 37, 77.

[16] "Distillation Studies." *Ind. Eng. Chem.*, 1926, **18**, 590-596.

[17] "Laboratory Distillation Analysis of Petroleum." *Ind. Eng. Chem.*, 1926, **18**, 64-67.

[18] "An Improved Laboratory Fractionating Column." *Ind. Eng. Chem.*, 1926, **18**, 826.

[19] "A 'Bubbler' Laboratory Fractionating Column." *Ind. Eng. Chem.*, 1926, **18**, 1093.

[20] *J. Inst. Petr. Techn.*, 1926, **12**, 586-590.

Review of Trade Journal Articles.

The following review of journal articles descriptive of distillation plants built and put in operation during 1926 or shortly before leaves much to be desired in the sense of being a comprehensive depiction of progress in the industry along these lines. Many of the most important plants that have been built are not included, for the reason that they have not been described in technical or trade journal articles. Such information as the writer has concerning some of them has been secured through confidential relationships with the companies themselves or manufacturers of the equipment used.

Notable advances have been made in the refineries of such large companies as the Tidewater Oil Co., Associated Oil Co., Tidal Refining Co., the Roxana Petroleum Corp., the Phillips Petroleum Co., the Anglo-Persian Oil Co., Ltd., the Magnolia Petroleum Co,. the Empire Refineries, Inc., the several Standard Oil Cos., the Atlantic Refining Co., and also in the refineries of many smaller but stlil progressive organizations. However, a review of these activities in their entirety, even if such were possible, would be so voluminous as in all probability to preclude its presentation in these pages.

F. C. Koch[1] describes the fractionation system used by the Medway Oil and Storage Co., Isle of Grain, Kent, for producing special naphthas from Russian kerosine. The charging stock is preheated from 56° F. to 250° F. by passing separate portions in heating exchanging relationship to the gas oil bottoms (476° F.) and the vapour (383° F.) from the second fractionating column. It then enters the stripping sections of the first column, leaves the base at 408° F., is heated in a pipe-still to 475° F. and partially flashed, whereupon the vapour so formed enters the base of the first column and the residual liquid is pumped to the uppermost of the stripping sections of the second column. The overhead product from the first column is 20·2 per cent. of a heavy naphthd boiling from 241° F. to 327° F. It is condensed, and the required portion returned as reflux to the top of the rectifier of the first column. The overhead from the second rectifier leaves at 383° F. and is a "white spirit" or mineral thinner. A portion is, of course, returned as reflux to the top of the second column. The heat into the base of the second column is supplied by vaporizing a portion of the column bottoms in a second pipe-still. The bottoms discharge from the pipe-still at 511° F. The 19·9 per cent., 44·7° Be. white spirit stream boils from 311° F. to 364° F. The 37·4° Be., 59·8 per cent. gas-oil bottoms boils from 397° F. to 628° F. Fuel consumption was 2·3 per cent. of the charge. The fractionation could have been made sharper had this been required.

[1] *Oil andGas J.*, Mar. 10, 1927, 135.

G. H. Reid[2] describes the distillation plant of the Jameson Oil Co. of Vernon, California. Pipe-stills and shell-stills are used. A heat exchanger preflash vaporizes 10-15 per cent. of the crude before it passes to the first pipe-still.

The plant of the MacMillan Petroleum Products Co. of Long Beach, California, is described by G. W. H. Reid.[3] The oil is preheated to 250° F. and flashed, thus removing about 10 per cent. as well as the water. The residuum from the pre-flash is pumped through a pipe-still and flashed in the base of a fractionating column. Kerosine and gasoline vapour leave the top of this column. The reflux is kerosine from the base of a second column. A heavy distillate is drawn from the lowest plate of the column and run to an auxiliary steam stripping column from the base of which stove oil is removed as a product. The vapour from the steam stripper is returned to the main column. The gasoline overhead from the rectifier is combined with the gasoline obtained in the preflash. Part of the kerosine from the base of the rectifier is used as reflux as stated and the balance is run to an auxiliary steam stripping column from the base of which kerosine of desired boiling range is removed. The vapour from the kerosine stripper is returned to the rectifier.

A second plant of the MacMillan Co. at Isom, Texas, is described by Neil Williams.[4]

The plant handles over 4000 barrels per day of Panhandle crude containing 2·0 to 2·5 per cent. sulphur, 2 per cent. salt water, and some sand. After being mixed with a small amount of caustic soda solution it enters a residuum heat exchanger at 80° F Leaving at 160-180° F. it flows to a horizontal baffled pressure type settling drum, where most of the salt water and sediment are eliminated. In flowing through a gas-oil and a second residuum heat exchanger the temperature of the crude is raised to 250° F., at which temperature it is flashed in a 4-feet diameter, 17-feet high tower. The unvaporized portion is pumped through a pipe-still, entering at 150-200° F. and leaving at 450° F., whereupon it is flashed in the uppermost stripping section of a combined stripping and rectifying column. Steam is introduced into the bottom of this tower to strip the descending residuum exiting at 430° F. Gas-oil is drawn from the base of the rectifier and stripped with steam in an auxiliary column, the vapour so removed being returned to the rectifying column. The combined gasoline and kerosine vapour from the top of the rectifier enter the base

[2] *Oil and Gas J.*, Mar. 25, 1926, 126.
[3] *Oil and Gas J.*, Aug. 5, 1926, 130-132.
[4] *Oil and Gas J.*, Mar. 24, 1927, 140-141.

of a second rectifying column from which a gasoline stream is taken overhead, and a kerosine, which is then steam stripped of its most volatile components in an auxiliary exhausting column, from the base. The overhead from the kerosine stripper enters the first flash tower. Appropriate reflux liquids are supplied to the top of each fractionating column by partially condensing the vapour leaving the top of each.

The plant of the Manhattan Oil Co. of Kansas City, Kansas, is described by C. O. Willson.[5] If the description given is correct as to details, this is a good example of building fractionating equipment that is far oversize as to diameter and number of plates used. The towers used on the shell-stills undoubtedly cost seven times as much as those actually required to do the work would have cost. The towers are not lagged, and reflux is supplied by wall condensation, a procedure that violates well established principles. The company also operates a pipe-still topping plant equipped with a fractionating tower.

The Marine Refining Corporation at Vernon, California, uses a single tower to cut eight streams. According to G. W. H. Reid[6] the crude is preheated in exchanger to 325° F. and flashed to remove a 61° Be. 375 E.P. gasoline. The residual oil at 280° F. enters a pipe-still, in which it is heated to 450 to 500° F. and then flashed. The vapours enter the base of a 4 ft. by 6 ft. by 42 ft. seven section Millif fractionating tower. Each section has its bubbler-cap plates, and outside down-pipes with weir controls. Each compartment is provided with cooling coils, heating coils, an open steam coil, and reflux admission means. The liquid from the base of each of the seven compartments constitutes a stream. The overhead is the eighth stream. The fractionation is not sharp, as can be seen from the distillation data given :—

	Gravity.	I.B.P.	20%.	50%.	90%.	E.P.
Preflash stream ..	61·5	105	—	—	—	337
Overhead	50·0	185	215	298	382	432
6 & 7 combined ..	44·9	265	317	352	415	450
4 & 5 combined ..	40·2	339	410	435	485	525
3 ..	38·6	365	420	455	510	550
1 & 2 combined ..	35·5	400	10% off at 480° F.			

The crude to the stills is 26-27° A.P.I., and contains 24·7 per cent. gasoline. The fuel oil residuum is 20° A.P.I. and 180° F. flash (Penaky-Marten closed cup).

The Panhandle Refining Co.[7] at Wichita Falls, Texas, distils topped crude to make gas-oil cracking stock, benzine, kerosine

[5] *Oil and Gas J.*, Nov. 11, 1926, 154-156.
[6] *Oil and Gas J.*, Feb. 18, 1926, 238-240. See also *Ref. and Nat. Gas. Mfr.*, Apr., 1926, 154-156 ; Nov., 1926, 29-32.
[7] *Oil and Gas J.*, Jan. 27, 1927, 32. *Ref. and Nat. Gas. Mfr.*, Mar., 1927.

and heavy residuum. The reduced crude enters the 2500 barrel pipe-still at 550° F., is heated to 840° F. under 175 pounds pressure, and then flashed in a 6 ft. × 30 ft. vaporizer with 5 stripping trays below the point of oil inlet and 6 ft. of spiral chemical tile. The vapour leaves the top of the vaporizer at 740° F., and enters the base of a 7 ft. 7-plate rectifier, where it is countercurrently contacted with reflux from a vapour heat exchanger through which the vapours from the rectifier pass. The top tower temperature is automatically controlled at 475° F. Gas-oil is removed from the base of the 5-plate stripping column that forms the lower part of the first tower. The overhead from the first tower enters a mid-point of a 6 ft. column with 13 rectifying plates and 5 stripping plates. Gasoline is removed overhead and kerosine is drawn as bottoms. Appropriate heat exchangers and coolers are used. The yields and nature of the several products are indicated by the following data :—

	A.P.I. Gravity.	% Yield.	I.B.P.	20%.	50%.	90%.	E.P.
Benzine ..	54	10	105	285	329	415	437
Kerosine ..	39–40	14	418	—	—	—	520
Gas-oil ..	29–30	55	520–540	—	—	680	—
Heavy residuum	12–14	20	—	—	—	—	—

Thus considerable cracking of the topped crude occurred. One interesting feature is the elimination of the free carbon in the residuum effected by introducing enough cold crude into the transfer line from the still to the vapourizer to drop the oil temperature 50° F. This temperature lowering sufficiently decreases the rate of decomposition to prevent appreciable decomposition in the vaporizer.

Clyde L. Smith[8] describes the distillation plant and procedure used by the Pure Oil Co. in several of its refineries. In a typical instance the fractionating columns are three in number. Each is 8½ ft. × 70 ft., with two horizontal cylinders of the same diameter and 16 ft. long placed at right angles to the axis of the tower, one at the base and the other near the top. The lower of these contains the reboiling coils and the upper the heat-exchanging and refluxing coils. Incoming crude oil passes in series through these three refluxing sections. Each is by-passed so that the volume of crude flowing through a particular refluxing section can be varied, and the top tower temperature thus controlled.

After leaving the last refluxing section the crude passes through the residuum exchanger and thence to one section of heating tubes

[8] *Oil and Gas J.*, Feb. 17, 1927, 38, 90. Presented before the New York meeting of the A.I.M.M.E., Feb., 1927.

in the pipe-still. It then discharges above the stripping section of the first tower. Gasoline is taken overhead. The stripped residuum from the flash is pumped back to the pipe-still, where it is heated to a higher temperature and discharged above the stripping section of the vaporizer. The unvaporized portion after passing the heat exchanger flows to storage as heavy fuel oil. The vapour enters the second tower. Either wax distillate or "charging stock" (gas-oil and wax distillate together) flows from the base of this tower through the reboiler coils of tower No. 3 and then to storage. The overhead from tower No. 2 is optionally a mixture of kerosine and naphtha, or gas oil, kerosine and naphtha. Naphtha is taken overhead. Kerosine or a light cracking stock composed of gas oil and kerosine is the stripped bottom product. Typical A.S.T.M. distillation curves of all products are given.

In an article mainly dealing with the peculiar difficulties encountered in running Panhandle crude Walter Miller,[9] of the Marland Refining Co., presents diagrams showing the lay-out of the single tower and three tower pipe-still units employed by this company. In the three-tower system the crude is flashed after the heat exchangers, and a rectified gasoline taken overhead in the first tower. The bottoms then are pumped through the pipe-still and flash in a second tower, from the base of which stripped residuum is removed. Combined gas-oil, kerosine and gasoline vapour is taken overhead to a mid-point of the third tower from which gasoline is taken overhead, kerosine from a plate some distance from the top, and stripped gas-oil from the base. All towers are of the most modern bubble type with cross-down pipes and high plate efficiency.

The single tower system is so arranged that gasoline, kerosine gas-oil and residuum are all removed from the one tower. There is nothing peculiarly remarkable about this, for the internal construction is such that the single tower comprises the rectifying and stripping sections required to do this. It is a matter of engineering choice whether one wishes to complicate the internal construction of a single tower or build several separate smaller towers to do a given job of fractionation. In general the smaller towers will be preferred, because of greater ease of erection and repair and lesser difficulty in making the plates level.

G. W. H. Reid[10] describes the plant and fractionation practice of the Hercules Gasoline Co. at Vernon, California. No unusual features are mentioned.

[9] *Ref. and Nat. Gas. Mfr.*, Jan., 1927, 47-54. *Am. Pet. Inst. Bull.*, Jan. 31, 1927, 309-314.

[10] *Oil and Gas J.*, Mar. 4, 1926, 186.

The topping plant of the Compania Ferrocarrilera de Petroleo of Buenos Aires is a pipe-still plant with special provision for handling a crude containing water.[11]

The Gilmore Oil Co., Vernon, California, uses[12] a pipe-still flash at 500° F., followed by fractional condensation to remove the gasoline from the crude. The bottoms from the partial condenser are run to a shell-still, where the kerosine is removed.

The Julian Petroleum Corp., Hynes, California, uses[13] a pipe-still plant equipped with partial condensers to effect fractionation.

C. O. Willson[14] describes the operations of the Amarillo Refining Co., pioneers in running Panhandle crude. There is nothing of particular importance in their fractionation procedure, but the difficulties encountered in handling this peculiarly corrosive and salty crude are of unusual interest.

Patents Issued during 1926.

The patents issued during any year are hardly an indication of the progress made during that year. Rather they are a reflection of the activities of a period two to five years previous. Nevertheless, they are of interest and importance.

In the following brief review of patents bearing on the fractionation of petroleum, sub-division of U.S. Patents into four groups has been made :—

(*a*) Vaporization Processes or Apparatus.
(*b*) Fractionating Columns.
(*c*) Fractionating Condensers.
(*d*) Fractionation Processes or Assemblies of Fractionation Apparatus.

Patents issued in other countries are fewer in number and are grouped together under the country of issue.

Vaporization Processes or Apparatus.

C. M. Alexander (U.S.P. 1,585,224, May 18, 1926) describes a process of vaporizing heavy oil in which the oil is heated to about 250° F., following which steam is introduced at a number of points along the heating conduit, thus causing a filming effect and also securing the benefit of the full partial pressure effect of the steam, since all vapour and liquid remain in contact until separated in a chamber provided for this purpose. The process

[11] *Oil and Gas J.*, June 3, 1926, 148.
[12] *Oil and Gas J.*, Jan. 21, 1926, 125-127.
[13] *Oil and Gas J.*, Dec. 31, 1925.
[14] *Oil and Gas J.*, July 22, 1926, 29, 141.

is applicable to the non-destructive distillation of heavy oils for the production of lubricating oil fractions.

E. M. Clark (U.S.P. 1,582,123, April 27, 1926) vaporizes petroleum from a series of stills, using steam or inert gas in each still in such manner that there is produced a 4 per cent. residual high melting pitch and overhead products substantially the same as those secured in coking the oil.

A. McD. Duckham (U.S.P. 1,568,886, January 5, 1926) fractionally vaporizes a material such as petroleum in a stepwise manner by causing it to flow in contact with metal baths at successively higher temperatures.

W. F. Faragher (et al, U.S.P. 1,601,729, October 5, 1926) describes a method of circulating oil in a still to prevent decomposition and render composition uniform. Appropriate baffles and introduction of a gaseous stirring medium are used.

C. F. Hanson and P. Vandervort (U.S.P. 1,597,375, August 24, 1926) vaporize petroleum by flowing it downwardly through a helical passage counter-current to ascending hot flue gas. Vapours are removed at several points.

F. M. Hess (U.S.P. 1,608,741, November 30, 1926) produces a series of vapours from petroleum by passing the oil counter-current to superheated steam in specially designed conduits.

F. M. Hess (U.S.P. 1,568,157, January 5, 1926) utilises the latent heat of the vapours and residuum to vaporize incoming crude oil.

F. A. Howard (U.S.P. 1,606,075, November 9, 1926) forms vapour from petroleum by passing it through a series of heating units, each of which comprises a pipe or conduit heater discharging on to the uppermost of several sloping shelves or trays within a shell-still. Steam is introduced into each of the heating coils and also into the body of oil in each of the shell-stills.

F. A. Howard (U.S.P. 1,594,957, August 3, 1926) describes a method of vapour formation in which petroleum is passed through six shell-stills in series. The steam introduced in the last three stills is recovered and used in the first three stills by a process involving condensation of the vapour from the last three stills to a point such that the steam content is 50 per cent. by volume, compressing this residual vapour-steam mixture, superheating it if desired, and introducing it into the first three stills.

W. Landes (U.S.P. 1,582,764, April 27, 1926) injects steam, natural gas, and crude petroleum into a chamber, and forms a light vapour. Cracking is claimed, but is out of the question at the temperatures cited.

L. E. Lee (U.S.P. 1,594,296, July 27, 1926) atomises oil into an internally heated still of frusto-conical shape.

W. K. Lewis (U.S.P. 1,599,824 and 1,599,825, September 14, 1926) describes an apparatus and process for forming vapour from petroleum oil when operating under a vacuum.

Percy Mather (U.S.P. 1,594,209, July 27, 1926) vaporizes petroleum by causing it to flow in a descending helical course, intercepting the liquid to form pools at successively lower levels, and shielding the vapours from direct action of the heat.

W. A. Schmidt (U.S.P. 1,604,424, October 26, 1926) forms vapour from petroleum in a manner designed to avoid thermal decomposition. The oil is flashed in a hot gas, entrained particles removed, the vapours mixed with a cool gas, and the resultant fog precipitated.

Fractionating Columns.

G. Egloff and H. P. Benner (U.S.P. 1,582,588, April 27, 1926) describe a so-called dephlegmator that is really a specially constructed sieve plate column from which down-pipes are omitted and the special feature of which is a variable number of holes in the plates from the top to the bottom of the column.

F. E. Gilmore (U.S.P. 1,598,772, September 7, 1926) claims a fractionating column, the special feature of which is several holes in the down-pipes drilled close to the upper side of the plates, so that water will not accumulate and freeze when the apparatus is not running.

W. W. Holland (U.S.P. 1,603,772, October 19, 1926) describes a fractionating column of which a 4 ft. diameter one comprising a number of plates spaced 12 inches apart and perforated with 3600 ¼-inch holes from each of which depends a ¼-inch tube 5 inches long is typical. The small tubes provide the only means for upward passage of vapour and downward flow of liquid. Above the top plate are placed several horizontal eliminator baffles for removing entrained liquid droplets from the vapour leaving the column.

R. B. Millard (U.S.P. 1,605,264, November 2, 1926) uses an equalizing device in "bubble-towers" or fractionating columns. The tendency of unequal vapour flow from the caps, resulting from poor construction or an unlevel condition of the column as a whole, is stressed. Liquid equalizing lines permitting flow of liquid from points of higher head to those of lower head can be used to correct such a condition and establish normal operation. Applications to standard types of cap columns are illustrated and a special form of trough column is also described.

R. B. Millard (U.S.P. 1,605,263, November 2, 1926) describes a bubble-tower with elongated liquid troughs and correspondingly

long caps and a liquid distributing trough beneath each plate to deliver the liquid to the troughs on the plate below.

R. B. Millard (U.S.P. 1,605,265, November 2, 1926) constructs a bubble-tower with a perforated wall forming the sides of an enclosed gas-receiving space. Superimposed trough plates extend around the inside and outside faces of the perforated wall. The reflux liquid is delivered to the uppermost trough. Catch plates or aprons are placed below each outer trough plate to deliver the overflow to the trough plate next below.

W. A. Peters, jr. (U.S.P. 1,601,320, September 28, 1926) controls the operation of a fractionating column automatically. The liquid feed is governed by a float actuated valve the float of which depends for its position on the pressure within the column. Overloading is thus prevented. The heat to the base of the column is thermostatically controlled. The total overhead is divided into reflux and product by a special adjustable weir that maintains the constancy of the division, no matter what the total quantity of overhead.

J. Schneible (U.S.P. 1,587,188, June 1, 1926) describes a fractionating column, the chief characteristic of which is a low pressure drop from the top to the bottom.

Fractionating Condensers.

A number of patents cover partial or fractionating condensers or processes of fractionating condensation. The relatively poor results securable by the use of such apparatus or processes as compared to the use of counter-current extraction methods scarcely warrants more than listing of these patents :—

F. B. Samuel	U.S.P. 1,571,805	Feb. 2, 1926
H. L. Allan	U.S.P. 1,572,374	Feb. 9, 1926
J. Young	U.S.P. 1,584,267	May 11, 1926
C. Matlock	U.S.P. 1,591,428	July 6, 1926
C. Jefferson	U.S.P. 1,609,822	Dec. 7, 1926
W. M. Cross	U.S.P. 1,612,265	Dec. 28, 1926

Fractionation Processes or Assemblies of Fractionation Apparatus.

W. C. Averill, jr. (U.S.P. 1,573,025, February 16, 1926, and U.S.P. 1,577,440), describes an apparatus and process for distilling petroleum, in which the oil is flowed over pans above the oil in the still, and the vapours so generated are passed through two packed fractionating towers in series. In the second of these towers condensate is formed by heat loss, or by introducing a water spray at the top, and the condensate, together with that collecting

in the base of the first tower, is pumped through a spray distributor located above the packing in the first tower. Excess condensate from the base of the first tower flows back to the still.

John E. Bell (U.S.P. 1,576,401, March 9, 1926) uses several shell-stills in series, and passes the vapour from each still except the first into heat exchanging and condensing conduits located in the preceding still. Partial condensers are also used to condense a portion of the vapour flowing from each still to the next preceding. This procedure results in the formation of a succession of near equilibrium fractions with partial vapour heat recovery.

Mark Benson (U.S.P. 1,607,043, November 16, 1926) discloses a process of combined fractionation and desulphurization in which petroleum oil, such as Persian crude, is vaporized in a single flash by mixing one part by weight of the oil with 0·9 parts of steam superheated to 750° F. to 1000° F. The vapours are passed in series through several fractionating towers, Feld scrubbers being preferred. In each tower the vapour is intimately contacted with the liquid from the base of the succeeding tower. In this manner a series of overhead fractions are secured. The large quantity of steam has the effect of hydrolyzing sulphur compounds that are finally removed as gas, dissolve in water condensed in the later stages of the operation, or can be removed by flowing appropriate reagents down the towers. Comparative data on sulphur contents of products made by this process and those made in the usual manner are given.

W. E. Chenot (U.S.P. 1,584,730, May 18, 1926) describes a process of distillation based on condensing a portion of the vapour and returning it to a vaporizing receptacle heated by the oil in the still. A number of such condensations and revaporizations can be used to secure the desired fractionation.

R. B. Chillas, jr. (U.S.P. 1,612,572, December 28, 1926) uses mechanical dividing boxes on the total condensed products from the top of a fractionating column, as well as upon the total liquid flowing at any lower point in the column, to maintain a constant division of any of these liquids into a product to be withdrawn and a second portion to be refluxed down the column. The total weight of vapour handled by the column is then without effect on the proportion of product and reflux at any point.

E. M. Clark and F. A. Howard (U.S.P. 1,595,642, August 10, 1926) distil petroleum by forming a series of vapours in a continuous battery of shell-stills, and fractionally condensing the vapour from each still by passing it through a series of partial condensers, the first of which is water cooled and functions as a boiler to deliver steam that serves as the cooling in the other partial condensers.

R. H. Crozier (U.S.P. 1,583,340, May 4, 1926, and U.S.P. 1,583,893, May 4, 1926) describes a fractionation process and apparatus involving heating of the vapour followed by cooling of the vapour by means of appropriate surfaces positioned within conduits through which the vapour is caused to flow.

L. Granger, C. Mariller and C. Prache (U.S.P. 1,574,622 February 23, 1926) utilize the latent heat of the oil vapour to form steam in specially arranged condenser boilers.

N. F. W. Hazeldine, (U.S.P. 1,580,372, April 13, 1926) describes a portable distillation equipment for petroleum.

H. M. Lamy-Torrilhon (U.S.P. 1,592,112, July 13, 1926) applies the principle of multiple effect evaporation to the operation of a fractionating column or other counter-current extraction device in which steam or other vapour is used in addition to other heating means at the base of each unit of the column.

T. W. Sowell (U.S.P. 1,593,107, July 20, 1926, and U.S.P. 1,609,667) builds a portable refinery mounted on railway cars in such manner that the essential units can be moved from place to place as required.

F. Tinker (U.S.P. 1,572,626, February 9, 1926) cools a portion of the oil from the base of a fractionating column and uses it to wash the tail-gas of the plant. The solution of low boiling components and oil is then used as reflux in the fractionating column, thus avoiding a separate redistillation plant.

M. J. Trumble (U.S.P. 1,586,130, May 25, 1926) uses petroleum vapour under pressure along with superheated steam to drive a turbine and thus generate power.

J. M. Wadsworth (U.S.P. 1,572,584, February 9, 1926) subjects petroleum to repeated vaporizing operations, combines and condenses fractions of similar boiling point, and redistils these primary condensates.

D. R. Weller and L. Link (U.S.P. 1,609,007, November 30, 1926) vaporize oil in a shell-still, pass the vapours through a series of partial condensers, return the bottoms from these condensers to the still out of contact with the vapours, and condense the vapour that passes all the partial condensers. When the still temperature has reached a point such that cracking occurs, wax distillate streams are diverted through coolers from the bottom of one or more of the fractionating condensers.

English Patents.

C. Ab-Der-Halden (E.P. 253,935, June 18, 1926) makes an addition to an earlier patent covering the continuous distillation of tar and like substances and the rectification of their by products.

The hot raw material is supplied below the surface of the liquid in the retort, so that the water contained in the feed can aid in the vaporization and distillation.

R. H. Crozier (E.P. 240,502, April 4, 1924) describes an apparatus for fractional condensation of hydrocarbon vapours. See also corresponding U.S.P. 1,583,340 and 1,583,893.

L. E. Hirt (E.P. 258,436, October 12, 1925) distils oil by passing it in thin films down tubes obstructed by baffles counter-current to steam or a stream of gas. In place of helical baffles the tubes can be packed with broken tile or similar material.

The Power Specialty Co. (E.P. 239,208, August 27, 1924) describes an apparatus for the fractionation of petroleum vapours by partial condensation.

A. Schmalenbach (E.P. 244,736, September 16, 1926) describes a process and apparatus for effecting vacuum distillation and fractionation of low boiling liquids. A condensate is first produced under vacuum and then fractionated under reduced vacuum corresponding to the charged vapour pressure relationships. Vapour not condensed in the condenser is absorbed in a liquid, so that it does not pass to the vacuum pump. Part of the pre-heated liquid is flashed into vapour under a vacuum corresponding to that in the fractionating column, and the vapour so formed introduced into the base of the fractionating column. The balance of the liquid flows to the stills.

The Société anon. D'Ougree-Marihaye (E.P. 239,502, September 8, 1924) uses a columnar apparatus for the fractional condensation of hydrocarbon vapours

C. Still and A. Kuhn (E.P. 264,735, July 20, 1926) use a fractionating column with radially placed caps and alternating central and peripheral down pipes.

Canadian Patents.

The following Canadian patents pertain to one phase or another of petroleum distillation :—

258,425	Feb. 23, 1926—	Pew, A. E., jr., and H. Thomas Mineral Oil Distillation.
261,666	June 15, 1926—	Crozier, R. H. Hydrocarbon Fractionation.
262,272	June 29, 1926—	Standard Development Co. Distillation Apparatus.
262,829	July 20, 1926—	Standard Oil Co. Distillation of Petroleum.
264,432	Sept. 21, 1926—	M. J. Trumble. Gasoline Production.

Cracking.*

By R. Pitkethly (Member).

During the past year the advance of knowledge, of the fundamental changes which take place when petroleum is subjected to the conditions of temperature and pressure existing in a cracking plant, has not been great. The subject is exceedingly intricate on account of the complex nature of the raw material and of the cracked product, whilst most of the research work undertaken has been done with the object of inventing or improving commercial plant for the purpose of producing motor spirit of a marketable quality irrespective of its chemical composition. Much of the knowledge of the composition of cracked oils has been gained either through work done in the attempt to account for and prevent knocking in internal-combustion engines or from investigations in connection with refining, which results in heavy losses when cracked spirit is treated in the same way as straight-run gasoline.

Nevertheless progress has been made by the ever-increasing body of research workers who have interested themselves in the problems of cracking and cracked products. Thermal decomposition is not now a sufficient definition of the term "cracking," as the process involves also the synthesis of innumerable compounds whose properties have not yet been investigated. The work of Fischer and others on the syntheses of alcohols and hydrocarbons by means of processes which may be considered within the limits of this section of chemistry have opened up the field of research and indicated the possibilities of cracking.

The activity in the production of new processes indicates the amount of work done in the effort to invent a practical process of high efficiency, without the faults of present-day plants.

The oil industry is vitally interested in the subject, not only on account of the economic value of cracking processes already in use but also because it appears to hold possibilities of more interesting development than any other section of the refinery.

From a commercial viewpoint the progress of cracking for the production of motor spirit has been remarkable, principally in the United States of America. The great expansion in that country has been possible for two reasons. It holds a market for gasoline of high final boiling-point for ordinary motor-car use, and there is an enormous production of natural gasoline, which is available for

* Paper received August 1st, 1927.

blending with cracked spirit to produce a mixture with the necessary volatility; cracked spirit invariably has a deficiency of low-boiling constituents which the natural gasoline supplies.

In Great Britain, where the specification for petrol requires a comparatively low final boiling-point, combined with a high volatility, cracking is not an economical proposition, as the yield of spirit to suit home consumption is not more than 50 per cent. of the quantity marketable under the American conditions. It is partly for this reason that there are not more than half-a-dozen cracking plants in this country.

In America, however, Navy gasoline with an end-point of 225° C. may be manufactured economically and a great expansion has taken place, for statistics show that the cracking capacity of refineries has increased 25 per cent. during 1926. The cracked spirit produced in 1926 amounted to nearly 9 million barrels, or 33 per cent. of the production from all sources. The increase alone during the year 1926 equalled the total production of cracked spirit in 1921. For the year 1926 the total spirit produced by cracking amounted to about 3,860 million gallons.

There is no uncertainty about these figures, and they remove any doubts as to the commercial value of the cracking processes in use at the moment. The number of refiners installing cracking plant steadily increases, and more than half the refineries in the United States are equipped with cracking plant of some kind, but the majority have adopted the Burton, Cross, Dubbs, Holmes-Manley, Jenkins, Fleming or Tube and Tank processes which account for most of the cracked spirit manufactured, and notwithstanding the innumerable patents which have been filed for the purpose of converting heavy oils into petrol, these processes maintain their position. The Holmes-Manley plant, which treats gas-oil only, appears to hold the record for long time running, without an enforced stop for the removal of deposited carbon. The Texas Oil Company have 100 units of this plant at their own works and 50 units in outside refineries. These units yielded 10½ million barrels during 1926.

Commercial plant tends to increase in size, in fact, at one refinery a unit is in course of construction, wherein the still has a measurement of 60 ft. long by 10 ft. diameter and the shell is of steel plate 3½ ins. thick. This is exceptional, as most other processes have standardised the size of the unit to process about 1000 barrels of oil per day.

Although the effect is not yet apparent, the enormous increase in crude oil production—*i.e.*, 1,950,000 barrels per day in January against 2,381,500 barrels per day in December, 1926—may have the effect of slowing down the development of cracking, as the

cost of production and refining the cracked product is greater than the cost of straight run spirit.

It is inevitable that the more costly process will suffer soonest, except in cases where a special brand of gasoline is manufactured, such as is obtained from the Holmes-Manley plant. The product of this process is a low end-point gasoline, which is treated in such a manner that the anti-knock value is not reduced.

The higher anti-knock value of cracked spirit in general, as compared with straight run spirit, may be in its favour, but this advantage will no doubt disappear as soon as the price of straight run spirit drops below the economical limit.

During last year no outstanding process of a fundamental nature has evolved, and most of the matter in the patent literature is concerned with improvements in methods of heating or arrangement of plant. A great deal of work runs in the direction of prevention or elimination of coke formation in plant of the usual cracking coil and expansion chamber type. The tendency is to eliminate the still or reaction chamber by cracking in tubular plant, thus reducing the capital cost and fire hazard whilst increasing the safety factor. Pipe stills are now used as combined topping and cracking units, whereby the yield of motor spirit is materially increased.

For the refining and desulphurisation of cracked spirit, sulphuric acid is still the most generally used reagent, notwithstanding the heavy losses, on account of polymerisation, removal of aromatics, and loss on redistillation, but some progress has been made in desulphurising by other methods. J. C. Morrell and G. Egloff[1] advocate revising the sulphur specification of gasoline as a remedy for this loss. In dealing with Californian cracked spirit, approximately 20 per cent. is lost with a reduction of 25 per cent. in the anti-knock value. They estimate that about 50 million dollars will be lost this year through the use of sulphuric acid refining alone in the United States, in order to meet the sulphur specification of 0·1 per cent. This loss is unnecessary, as tests have proved that motor engines show no signs of corrosion after running under normal conditions on a spirit containing 0·4 per cent. sulphur. Technical men are unanimous in condemning the sulphur specification as it stands.

Gray's[2] method for refining cracked spirit in the vapour phase, with the elimination of the sulphuric acid treatment, has developed somewhat during last year, as there are now sixteen commercial installations in use or under construction.

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[1] *Ref. & Nat. Gas Manf.*, **6**, 2, 78.
[2] *Journ. Inst. Petr. Tech.*, 1925, **11**, 21A.

Some of the processes patented recently are of questionable value, and a great many consist fundamentally of the principles of processes already in use, but differ in detail. Many of these details are ingenious or the application is novel.

In dealing with an oil such as Panhandle crude G. Egloff and J. C. Morrell[3] suggest cracking it on the field to overcome difficulties due to the high setting point, particularly in cold weather. A yield of 60–70 per cent. of Navy gasoline may be obtained.

C. M. Alexander[4] sprays heavy oil into a large body of oil which is maintained at a high temperature and is energetically agitated. The heavy oil is circulated through a settling chamber wherein the carbon is deposited.

J. E. Bell[5] regulates the pressure in pressure stills by means of a fixed orifice in conjunction with a regulated partial condensation at still pressure.

R. B. Day[6] claims a process consisting of a vessel which acts as preheater and an expansion chamber, which is connected in series to a number of tubes superimposed horizontally in a furnace. Each tube is furnished with a shaft and paddles. The oil passes downwards through the tubes and gradually increases in temperature. The residue and carbon are removed whilst the vapours return through the preheating vessel, through the dephlegmator into the cooling system.

W. T. Hancock and M. Boyle's[7] apparatus consists essentially of a still having longitudinal perforated tubes supported by end-plates which are spaced from the ends of the still. Superheated steam at 1500 lbs. pressure is passed through the tubes into the oil space. The steam supplies the heat to crack the oil.

H. R. Berry[8] treats hydrocarbon oils with superheated steam at cracking temperature to form oxides of carbon and hydrogen. The steam is introduced in such a way that it forms a blanket between the hot walls of the plant and the oil. Hydrogenation is claimed.

E. M. Clark[9] heats petroleum to decomposition temperature and the evolved vapours are allowed to pass into contact with a separate body of oil maintained at a lower temperature whereby condensation is effected. The oil displaced by condensates is fed back to the first still and the pressure is regulated by releasing permanent

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[3] *Petroleum Times*, **14**, 203.
[4] *U.S. Pat.* 1,573,532.
[5] *U.S. Pat.* 1,575,031. *Journ. Inst. Petr. Tech.*, 1926, **12**, 68A.
[6] *U.S. Pat.* 1,570,131. *Journ. Inst. Petr. Tech.* 1926, **12**, 108A.
[7] *U.S. Pat.* 1,576,742.
[8] *U.S. Pat.* 1,569,532.
[9] *U.S. Pat.* 1,578,802.

gases which are passed through a condenser refluxing into the second still.

G. Egloff[10] suggests an externally heated still with means for producing an electric arc simultaneously within the charge of oil, thus heating to a cracking temperature.

F. E. Wellman[11] cracks by circulating oil through a series of pipes arranged in pairs and heated in a furnace. When 50 per cent. of the oil has passed out of the circuit as distillate the residue is blown out of the tubes and a new charge injected.

A very rapid circulation of oil is obtained by R. E. Humphreys[12] in a cracking plant consisting of an upper and lower container connected to each other by a number of short pipes along each side. The upper container has a vapour outlet, and the lower is connected at the forward end to a transverse drum by a conduit. A second drum lies beneath the other end of the container and is connected to the upper drum by upwardly inclined tubes which pass through the heating chamber. A second conduit connects the lower drum to the rear end of the container. The drums and containers are exterior to the heating chamber.

J. W. Coast[13] continuously distils and cracks petroleum oils by heating in a horizontal still under pressure. The still is fitted with a scraper which conveys any coke formed to one end of the still, whence it is withdrawn together with a certain amount of heavy oil into a coke settling chamber. The heavy residue is drawn off periodically and the lighter constituents pass into an exchanger, where they mix with the incoming cracking stock. A vapour line from the expansion drum conveys distillate to gasoline receivers.

A. J. Paris, jun.,[14] puts forward a process and apparatus wherein gas and oil are mixed, heated, and compressed until the desired change has taken place.

G. E. Heyl[15] cracks mineral oil to finality in an apparatus composed of a plurality of stills with separate dephlegmators disposed in series. The condensate from each dephlegmator passes into the next (forward) still of the series. Temperatures are maintained from 600° C. to 1000° C. The oil is thus repeatedly cracked at successively higher temperatures until the entire bulk is decomposed.

F. Lamplough[16] mixes oil and naphthalene and pumps the mixture through two heated coils. The larger coil has a specially

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[10] *U.S. Pat.* 1,579,601.
[11] *U.S. Pat.* 1,581,895.
[12] *U.S. Pat.* 1,582,929.
[13] *U.S. Pat.* 1,585,233.
[14] *U.S. Pat.* 1,585,687.
[15] *E.P.* 259,493.
[16] *E.P.* 258,656.

designed valve which operates intermittently and discharges the products into a cooler.

F. A. Howard[17] uses mercury vapour, to heat the oil to be cracked, in a jacketed still.

E. O. Linton[18] combines a vaporising still and a cracking retort. Oil is passed over inclined plates in the upper part of the still, and residue is withdrawn at the bottom. The vapours from the still pass through an expanding nozzle into a cracking retort, thence to the condensing system.

J. W. Lewis[19] combines a vertical still and a pressure still with a tubular heating structure. The upper and lower ends of the heating tubes are connected at different levels to the vertical still. These connections may be controlled by means of valves. Pressure is maintained on the stills and tubes.

G. Egloff and H. P. Benner[20] propose to crack mineral oils in an apparatus consisting of a stationary still situated above a rotary still within a furnace. The temperature of the stills can be regulated independently, and they are connected to each other by a transfer line. Vapours pass from the upper still to the dephlegmator and condenser. The lower still may be rotated continuously or intermittently. Charging stock may be delivered into either or both stills and the reflux may be returned to either still. The temperature may be varied and differential pressure may be maintained on the stills.

L. B. Cuddy[21] claims an apparatus in which the still is so constructed that the heating gases pass around the top of the still and flow downwards. The still is fitted with scrapers to remove carbon, which falls into a conical bottom and is periodically removed.

D. L. Thomas[22] has devised a still on the Venturi tube principle, wherein converging and diverging sections are connected by a throat-piece of special construction. Two reactions are involved in the cracking process. Firstly, decomposition takes place, and diminished pressure assists this action; secondly, condensation and hydrogenation occur and increased pressure increases this effect. It is claimed that these conditions are obtained by means of this invention.

G. Egloff and H. P. Benner[23] place a nest of tubes between a pair of headers and within a furnace. The oil is cracked in the tubes

[17] *U.S. Pat.* 1,586,994.
[18] *U.S. Pat.* 1,592,214.
[19] *U.S. Pat.* 1,593,905.
[20] *U.S. Pat.* 1,595,179.
[21] *U.S. Pat.* 1,598,805.
[22] *U.S. Pat.* 1,611,615.
[23] *U.S. Pat.* 1,617,619.

and passes into an expansion chamber so designed that the vapours enter at the top, travel to the bottom, then ascend upwards to the dephlegmator. Carbonaceous matter is constantly drawn off from the bottom of the expansion chamber by means of a rotary valve, whilst the reflux from the dephlegmator is directed into the cracking tubes.

The anticipated revival of vapour phase cracking for the purpose of manufacturing anti-knock hydrocarbons has not materialised, but patents still appear in connection with this branch of the industry. L. Clark[24] endeavours to overcome the objectionable features of modern cracking plant by conducting operations without pressure. The oil is introduced directly into contact with hot gases from the furnace. The carbon produced by cracking is flocculent, and is periodically blown out in a condition similar to carbon black. It is claimed that there is 100 per cent. contact between heating gases and oil vapours, there are no high pressures calling for expensive equipment, there is a minimum of fire risk and possible danger to life, the by-products are marketable and the operation is continuous. The losses are not stated, but 40 to 60 per cent. conversion is claimed.

F. C. Van de Wahr and F. R. Sunderman[25] surround the cracking tube by a larger protecting tube and claim that very precise temperature control may be obtained by circulating cool air through the protecting element as necessary.

J. H. Adams[26] preheats the charging stock under pressure to the boiling-point, then expands it into a converter wherein cracking is accomplished.

Work on the application of electric energy for the purpose of cracking oils has been done by L. B. Cherry[27], who subjects the oil to cracking temperature while it is transversed by an ionising current flowing from anode to cathode.

D. L. Thomas[28] subjects unsaturated compounds, produced by cracking heavy oils, to the silent discharge of a high tension current whilst under high temperature and pressure conditions.

C. N. Page[29] provides an apparatus wherein a high voltage, high frequency current is used to crack petroleum. The arrangement of wires and rods and the nature of the current produces an oscillating magnetic field which causes a high molecular tension, with the result that decomposition takes place with greater ease.

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[24] *Ref. de Nat. Gas. Manf.* 5, 4, 37.
[25] *U.S. Pat.* 1,567,212.
[26] *U.S. Pat.* 1,585,355.
[27] *U.S. Pat.* 1,588,306.
[28] *U.S. Pat.* 1,585,573.
[29] *U.S. Pat.* 1,597,476.

O. P. Amend[30] heats heavy oils by means of massive electric resisters contained in a pressure still.

A large amount of work on catalytic processes and materials has been done during 1926, possibly as a result of Fischer's successful application of catalysis in the production of alcohols and hydrocarbons. The Sinclair Refining Company[31] reduce the rate of carbon formation in cracking stills by circulating the oil through a mass of metallic oxides deposited on a bed of filtering material, the whole being contained in the still.

G. Egloff and H. P. Benner[32] simultaneously crack and refine by causing the vapours of the oil to traverse a bed of fuller's-earth or other catalytic material which is placed in the vapour space of a cracking still.

L. Edeleanu[33] converts heavy oils into light products by distilling them with a "double compound" of aluminium chloride and hydrocarbons.

R. Cross[34] treats petroleum by vaporising under pressure and passing the oil vapours through a mixture of Benbonite, diatomaceous earth and a salt of a metal—*e.g.*, copper for removal of sulphur compounds.

G. L. Prichard and H. Henderson[35] pump a mixture of oil and aluminium chloride through a coil immersed in a molten lead bath. The hot mixture is released into a chamber to vaporise the spirit and separate the heavy oil from the aluminium sludge.

G. W. Wallace[36] passes oil vapours over carbon and a catalyst such as nickel, and T. Suguyoshi Mii[37] uses aluminium hydrosilicate impregnated with a soluble chloride as a catalyst.

P. Danckwardt[38] pumps oil and hydrogen through a number of vertical tubes, connected in series. The oil is heated to a temperature not exceeding 430° C., and maintained at a pressure of from 400 to 1000 lbs. per sq. in. The cracked oil enters a separator where heavy residue condenses and mixes with fresh stock. The uncondensed vapours are led through molten sodium hydroxide in which nickel or other catalyst is suspended. Thereafter the vapours are condensed.

Cracking and simultaneous hydrogenation of oils is claimed by

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[30] *U.S. Pat.* 1,613,735.
[31] *E.P.* 246,116, 232,178, 241,866.
[32] *U.S. Pat.* 1,569,855.
[33] *U.S. Pat.* 1,586,357.
[34] *U.S. Pat.* 1,587,491.
[35] *U.S. Pat.* 1,585,263.
[36] *E.P.* 255,159.
[37] *U.S. Pat.* 1,590,640.
[38] *U.S. Pat.* 1,594,666.

G. Kolsky[39], who heats, under pressure, a mixture of oil, ammonium chloride, and finely divided iron or other metal. The iron chloride and ammonia formed are caused to react to recover ammonium chloride.

J. H. James[40] passes hydrocarbon vapours and air over the oxides of molybdenum, vanadium or uranium at a red heat. The partially oxidised product is cracked in the vapour phase in contact with iron, nickel, copper or basic oxides.

C. D. Mazo[41] simultaneously hydrogenates and desulphurises oils by passing the vapours and steam at atmospheric pressure over metals capable of decomposing water.

In the Wade[42] hydrogenation process superheated water is injected with the oil into coils of tubing and subjected to cracking temperature. In the last coil the vapours come into contact with the catalyst, stated to be a chrome-nickel alloy, and an almost instantaneous reduction of temperature takes place. Motor spirit of high anti-knock value is made.

H. J. Lea and C. W. Humphrey[43] treat heavy oil with aluminium chloride produced "in situ" by distilling the oil in a current of chlorine. The mixture of gases are led into a chamber containing alumina, and the products of the reaction pass to a digester.

J. B. Weaver[44] cracks oils in the vapour phase in the presence of steam and ferric oxide, and M. Melamid[45] sprays oils by means of hydrogen into molten tin, antimony or bismuth, whilst H. R. Moody[46] maintains the oil in contact with aluminium carbide for a length of time.

The great increase in the use of cracking plant during the last few years has brought the industry face to face with the question of corrosion of plant which is operated under high pressure, with consequent liability to give way under working conditions and lead to loss of life and property unless very carefully supervised. The need for investigation has resulted in a considerable gain of knowledge on the subject, and many methods for the protection of plant.

G. Egloff and J. C. Morrell[47] contribute an article on corrosion of cracking plant. Tests were made with a Californian oil containing 1 per cent. of sulphur over a period with various metals suspended in the vapour zone of a commercial cracking unit.

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[39] *U.S. Pat.* 1,598,973.
[40] *U.S. Pat.* 1,597,796, 8.
[41] *E.P.* 263,381.
[42] *Ref. & Nat. Gas Manf.* **5**, 11, 24.
[43] *U.S. Pat.* 1,606,246.
[44] *U.S. Pat.* 1,601,786.
[45] *U.S. Pat.* 1,602,310.
[46] *U.S. Pat.* 1,601,406.
[47] *Oil & Gas. J.* **25**, 140.

Aluminium resisted the action of sulphur most and copper least. Mild steel does not last long under high temperature conditions, but a steel containing 15 per cent. chromium resists sulphur corrosion remarkably well. Chromium plating if properly done resists corrosion remarkably well. Lining the plant with aluminium is not satisfactory owing to its low softening point and high coefficient of expansion. Calorized tubes are inconsistent; sometimes they stand the action well and sometimes the calorized tubes fail as rapidly as ordinary mild steel.

K. V. King[48] patents the plating of the interior surface of cracking retorts with chromium.

The treatment of cracked products for the production of marketable gasoline remains in much the same position as at the beginning of the year, but on the research side a considerable amount of work has been done to determine or to improve methods of determining the constituents of cracked spirit.

J. S. S. Brame[49] contributes information regarding the action of sulphuric acid, 85–88 per cent. strength, on cracked spirit and on spirit with a proportion of added toluene. The results confirm Brochet's work, as a serious loss of toluene occurs with either acid.

J. C. Morrell[50] refines cracked spirit by washing with acid and soda in the usual way, then treating with calcium magnesium or aluminium sulphide suspended in water.

G. Egloff and H. P. Benner[51] describe a method of producing sweet water-white spirit by distillation in the presence of caustic soda and fuller's-earth.

A. McD. McAfee[52] treats cracked spirit with aluminium chloride in the presence of gases from the cracking plant to yield spirit of any desired degree of saturation.

W. R. Ormandy and E. C. Craven[53] contribute further information on the action of sulphuric acid on unsaturated and aromatic compounds. They come to the conclusion that aromatic compounds may be determined by their sulphonic acids formed by reaction with 98 per cent. acid. Amylene and heavier olefins in cracked spirit, when treated with sulphuric acid, yield large proportions of saturated compounds of higher boiling-point and not olefin polymers, as has been hitherto assumed. Aromatics are not entirely removed

[48] *U.S. Pat.* 1,582,407.
[49] *Journ. Inst. Petr. Tech.*, 1926, **12**, 221.
[50] *U.S. Pat.* 1,569,872.
[51] *U.S. Pat.* 1,608,089.
[52] *U.S. Pat.* 1,608,329.
[53] *Journ. Inst. Petr. Tech.* 1927, **13**, 311.

by sulphuric acid, but partly condense with the olefins present in the cracked spirit. The acid liquor from amylene contains very little amyl-hydrogen sulphate.

'Anti-Detonators.' *

By G. B. Maxwell, M.C., Ph.D., B.Sc.

No review of the past year's work on anti-detonators—a loose term which, however, has passed into general usage—would be complete without a short summary of the prevalent theories of pinking in the internal-combustion engine.

One popular theory holds that the trouble is caused by the incidence of a pressure-wave on the cylinder walls and piston-head due to a sudden flame acceleration of the nature of a true detonation-wave. Such an acceleration is variously attributed to the activation of so far unburnt mixture by radiation or by electrons from the burning portion. According to this view the action of anti-detonators is to prevent the production of the detonation-wave either by absorbing the radiation or by preventing the ionization of the unburnt charge.

In England the idea of "self-ignition," associated with the names of Ricardo and of Tizard and Pye, has gained much support. This view attributed the "pink" to the heating and compression of a portion of the unburnt charge by the expanding, burning portion, thus causing the former to ignite spontaneously throughout its bulk and give a very sudden pressure increment.

For the purpose of this review the term "anti-detonator" is held to include all substances which when added to a pinking fuel—usually a paraffin-base petrol—raise the permissible compression-ratio of a given engine without seriously detracting from the performance of the fuel or causing undue wear and tear in the cylinder. Thus straight diluents, such as aromatic and naphthenic hydrocarbons and organic amines, are included together with "negative catalysts" like various organo-metallic compounds and some elements and metal sols.

During 1926 a much clearer understanding of the mechanism of "anti-knock" has emerged. The nuclear hypothesis of Callendar, King and Sims[1] has placed the self-ignition theory of pinking on a more rational basis. This latter theory did not give

* Paper received July 12, 1927.

[1] *Engineering*, 1926, **121**, 475, 509, 542, 575.

a satisfactory explanation of the violent disturbance in a pinking engine, since the ignition of a gas mixture by compression was known to start from a point or layer and spread throughout like a normal combustion. Further, the addition of anti-detonators to the mixture was not found to affect the ease of ignition by compression.[2] Callendar has shown the possibility of the presence in an engine cylinder of numbers of high-boiling inflammable liquid nuclei, the sudden self-ignition of which would cause the observed effect. That the ignition of such liquid nuclei is inhibited by anti-detonators seems clear from the work of Egerton and Gates.[3] They have shown that there is a close parallel between the effect of a particular substance on the ignition temperature of a fuel (as determined by the Moore hot crucible method, but in contact with air, not oxygen) and its anti-knock value in an engine using that fuel. The manner in which the ignition of the liquid nuclei is brought about and the action of the anti-detonator in inhibiting the ignition have to some extent been explained in a second series of papers by Callendar.[4] Incipient oxidation of pinking fuels was remarked at much lower temperatures than with non-pinking fuels. The products were found to contain traces of highly oxygenated substances, believed to be organic peroxides, particularly if the fuel were in the form of a mist or spray. Since organic peroxides are generally unstable explosive substances which are readily decomposed by finely-divided metals, the rôle of anti-detonators like lead tetraethyl may be to decompose the peroxides as fast as they are formed. This view is in accord with the discovery of Mardles and Sims[5] that a given metal which is effective in the combined form—*i.e.*, as organo-metallic compound—is equally efficient uncombined when added in colloidal suspension. It should be recorded, however, that Olin, Read and Goos[6] have disputed the validity of this discovery.

These researches have all been based on the theory that pinking is due to the spontaneous ignition of unburnt charge in the cylinder. In the main it can be claimed that the results have supported this view and have cleared away some of the difficulties in accepting it.

There remains the considerable amount of work which has been done to test the "detonation" theory of pinking. It has long been known that paraffin-air mixtures would not detonate in a vessel of the size of an internal-combustion engine cylinder when ignited at normal temperatures and atmospheric pressure. There remained

[2] Pignot, *Comptes rend.*, 1926, **182**, 376.
[3] *Journ. Inst. Petr. Techn.*, 1927, **13**, 244.
[4] *Engineering*, 1927, **123**, 147, 182, 210.
[5] *Engineering*, 1926, **121**, 605.
[6] *Ind. Eng. Chem.*, 1926, **18**, 1316.

the possibility that a higher initial pressure and temperature would shorten the length of normal flame travel required before the detonation-wave was set up. This possibility has been confirmed, as regards higher pressures, by Dumanois and Laffitte.[7] Egerton and Gates[8] have, however, shown that the addition of anti-detonators has no effect on the ability of various mixtures of acetylene and pentane with air to set up the detonation-wave. Their experiments were carried out at various initial temperatures and pressures and do much to confirm the scepticism towards the "detonation" theory felt by all those workers who have had any experience of the true detonation-wave. This scepticism is not decreased by a consideration of the work of Charch, Mack and Boord[9] on the electrical conductivity of the exploding charge in an engine cylinder and of the effect of anti-detonators thereon. These workers concluded that increased ionisation was just as likely to be an accompaniment as a cause of pinking. The results of Garner and Saunders[10] on the lowering of the conductivity of an inflaming hydrogen-oxygen mixture in a closed cylinder by the addition of anti-detonators are more difficult to interpret. Both with and without the anti-detonators the flame-speeds were the same, so the action can hardly be a pure temperature effect.

The effect of anti-detonators on the radiation from an engine-cylinder charge has been examined by Clark and Thee[11] and Henne and Clark.[12] During pinking the flame spectrum was found to undergo an extension in the ultra-violet, whilst the addition of anti-detonators suppressed the pinking and restored the normal spectrum. Again the phenomenon appears to be an effect rather than a cause of pinking.

A startling claim was put forward in 1926 by Dumanois.[13] By means of his "stepped piston" Dumanois is said to have raised considerably the permissible compression-ratio in a given engine using a paraffin-base fuel. This invention does not come under our definition of "anti-detonators," but it is thought well to mention it as so far the claims made for it have not been substantiated.

This last remark also applies to the fuel "Gasin."[14] The inventor, G. Grote, believes that pinking is due to the sudden detonation of the cylinder charge, either before or after the passage of the spark owing to the electrification of the charge during induction.

[7] *Comptes rend.*, 1926, **183**, 284.
[8] *Proc. Roy. Soc.*, 1927, **114**, 137.
[9] *Ind. Eng. Chem.*, 1926, **18**, 334.
[10] *Faraday Soc.*, Oct., 1926, p. 335.
[11] *Ind. Eng. Chem.*, 1926, **18**, 528.
[12] *Comptes rend.*, 1927, **184**, 26.
[13] *Comptes rend.*, 1926, **182**, 1378.
[14] Reported in the *Chemical Age*, 1926, **14**, 433; **15**, 181.

In the preparation of "Gasin" electrically conducting substances are added to the basic fuel. This hypothesis of pinking does not explain the action of such anti-detonators as lead tetraethyl, but cannot be dismissed as wholly fanciful in the light of the known effect of electrification on the formation of fogs and mists.

In conclusion it can be stated that the period under review has produced some work of outstanding merit in this field of investigation. The most profitable lines of attack on the subject have been greatly reduced in number, and the way is clearly marked for further study.

Lubricants.*

By HAROLD MOORE, M.Sc.(Tech.), A.I.C., F.C.S., A.I.Mech.E. (Member.)

THE year 1926 has shown steady development, but no remarkable changes in technique or in the economics of lubricants have taken place. The year throughout was one in which the production of crude oil exceeded the requirements, and in consequence it has been a period of low and falling prices. It is of interest to note that ever since the end of the boom which followed the War, if one ignores small fluctuations, the price of all classes of lubricants has been steadily falling. Both the steadiness and the amount of fall have been much more pronounced in the price of lubricants than in the price of other petroleum products.

It is probable that this may be explained by the fact that the development of new technical processes has had much more influence in the production of lubricants than in the production of other petroleum products, and also the comparatively high prices at which lubricants were sold during the boom period were such as to allow of great reductions in price.

Though outside the period dealt with in this review, it may be of some utility to look back over the general movements and tendencies which have been obvious during the last seven years.

For some time after the Great War the conditions in the Russian oil industry were such as prevented this field entering seriously into the lubricating oil market. The preparation of lubricants from fields other than those in the United States was not sufficiently developed for this production to have any noticeable effect on lubricating oil prices. The main source of cylinder stocks, both filtered and dark, was the Pennsylvanian field, whilst distillate

* Paper received July 30, 1927.

lubricants were being manufactured in fair quantities in the Mid-Continental, Californian, and Texas fields. As nearly all oil fields supply petrol, kerosene, gas oil, and fuel oils, it will be noted that the sources for the production of lubricants were much more limited than those for the production of the less highly refined products. The last six years has, however, seen a very great change in the position.

Russia now supplies a very large quantity of high quality lubricating oil distillates, together with a small amount of cylinder stocks. Lubricating oil distillates, both of asphaltic and paraffin base, are now being prepared from the crude oils of the majority of oil fields. Venezuelan pale and red oils are used in large quantities in this country, while Persian oil is now being worked at Llandarcy for lubricating distillates, cylinder oil and long residuum. The Mid-Continental field of the U.S.A. is now the largest producer of both filtered and dark cylinder oils and the "Western" cylinder oils of both classes have met with very considerable success. The widening of the field of lubricating oil production has resulted in greater competition, greater variety in the products available, and in reduced prices. Returning to the developments of the year 1926 we observe that the "Western" (Mid-Continental paraffin base) dark cylinder oils, have still further entrenched themselves in the cylinder oil market. The "Western" dark cylinder oils were regarded with great suspicion when they first entered the market, and there was a few years ago much room for criticism of these stocks, as they were very poorly refined, possessed high asphaltum contents, dark colour and high cold test. The last five years has, however, seen very great improvement in these properties, these oils now being usually as free from asphalt as the corresponding Pennsylvanian oils, whilst their colour and cold test leaves little to be desired. Their viscosity-temperature curves are, as one would expect, steeper than those of Pennsylvanian dark cylinder stocks.

The "Western" filtered cylinder oils are now recognised constituents of practically all the high-viscosity motor oils, the comparatively high price of Pennsylvanian cylinder oils debarring their use in the more popular brands. The colour and cold tests of the "Western" filtered cylinder stocks have shown great improvement, the former due to wider use and greater experience in the contact clay processes, and the latter due to the adoption of the Sharples de-waxing process. The entry of Pennsylvanian long residua into the British lubricating oil market in appreciable quantities commenced in 1925, and the year 1926 saw an increase in the use of these oils, together with the entry into the British market of long residua of Mid-Continental origin. The "Western" long residua possess properties

similar to those of the Pennsylvanian long residua, but are higher in specific gravity and steeper in their viscosity-temperature curves. They are also, on the average, a little lower in flash point. Lubricating oils of Persian origin are now becoming better known on the market. They possess high specific gravities, very high flash points (probably due to close fractionation) and reasonably good viscosity-temperature curves.

The Oxidation of Lubricating Oils.

There is a great necessity for a standardised oxidation test for lubricating oil, and although innumerable tests have been put forward, there is no particular test which is recognised as the official method of determining the tendency towards oxidation of a mineral lubricant. The Michie sludge test has received general recognition in this country as a method of testing the tendency towards oxidation of transformer oils, but it is doubtful whether the results are of such a nature as to be of great value when applied to lubricants. The test is also very elaborate and lengthy, and consequently not one which is likely to come into general use for the lubricating oil trade. A new test for determination of the tendency to oxidise has recently been devised by the Committee of the British Engineering Standards' Association in connection with P. 4 specification for the supply of mineral lubricating oils for aircraft engines. Although the test has recently undergone alteration, and the conditions to be employed in the test are by no means finally decided, it has already received a certain amount of recognition by the lubricating oil trade, and it appears possible that at some time in the future this may become the recognised oxidation test for mineral lubricants. The test is of shorter duration than the Michie sludge test and it has more bearing on problems connected with lubrication.

It must be borne in mind that the Michie sludge test consists of oxidising the oil and then determining the hard asphalt generated by the oxidation, whereas the test employed in the P. 4 specification is one in which the viscosity of the lubricant is determined before and after oxidation and in which the coke value is also determined before and after oxidation.

Moore and Barrett[1] have used the Air Board method of oxidation in some investigations on the oxidation of lubricating oils of various bases. Russian, Californian, South American, Pennsylvanian and Texas oils have been investigated, their viscosities being determined before and after oxidation, whilst the coke values and acidity have also been determined before and after blowing. Other

[1] *Journal Inst. Pet. Tech.*, 1926, **12**, 582.

determinations have also been made on the lubricants and the sludge value according to the Michie test has been taken. The results indicate that the Pennsylvanian long residuum exhibits extreme stability. The Russian oils are very nearly as stable as the Pennsylvanian, whilst the so-called ashpalt base oils, Californian and Texas, come out comparatively poorly, and the South American red oil shows an extremely large increase in viscosity and a very high coke value after oxidation.

It is interesting to note that these results are very closely related to the sulphur content of the oils, the best results being given by the oils of lowest sulphur content.

Moore and Barrett claim that the most important feature governing the use of oils in internal combustion engines is the generation of sludges by oxidation.

Staeger[2] criticises the Michie test as a method of determining the suitability of transformer oils and claims that the B.B.C. test, in which the oil is heated to 112°C. for 300 hours, agrees best with the results of actual service. Staeger considers the temperature of 150°C. used for Michie test as too high.

Musatti and Pichetto[3] have made experiments with a view to devising a sludge test more in line with actual practice and employed copper cups of specified dimensions heated by air ovens or oil baths for very prolonged periods, free access of air being permitted. As a result of their experiments the authors conclude that the iodine, bromine and formalite numbers of the oils are no measure of its tendency to oxidise, but that the proportion of oil extractable by liquid sulphur dioxide can be used as an estimate of the tendency towards oxidation.

Dover and Cromwell[4] have investigated the co-efficients of static friction of oxidised lubricants by means of a Deeley machine, the lubricants having previously been oxidised with ozone.

Marshall and Barton have made laboratory experiments on a petrol engine with a view to determining the correlation between practical results and laboratory tests. They claim that the tendency to oxidise possessed by the various asphalt base oils does not affect their operation in the engine. The proportion of carbon formed on the piston top is very closely related to the coke values of the oils before use.

A very large number of patents have been taken out on the subject of the contact clay filtration process. There is every indication that the use of this process is going to be developed by innumerable

[2] *Ind. Eng. Chem.*, 1925, **17**, 1272.
[3] Ann. Chim. Applicata, 1925, **15**, 238.
[4] *Ind. & Eng. Chem.*, **1**, 94.

patents, the majority of which show lack of originality in very much the same way as is the case on the subject of cracking. The number of patents which have been taken out on this subject and the number of papers which have been read on the subject of contact clay filtrations are so great that it is quite impossible to attempt a review of them in this report.

The possibility of preparing lubricating oils from coal has been the subject of a paper in "Engineering,"[5] in which results from L. & N. low temperature carbonisation plant are given. The lubricants referred to in this paper have been prepared by direct distillation with hydrogenation. It may be pointed out that hitherto lubricants prepared from coal commercially have met with little success. The theory of lubrication has been the subject of a paper by Dr. Ormandy[6] read before the Institution of Chemical Engineers.

Becker[7] has investigated the thickness of various oil films and has put forward a general equation from which the film thickness can be determined from the load, speed and viscosity. Experimental evidence is given to prove the correctness of the formula.

Wilson and Wilkin[8] discuss the problem of employment of equilibrium oils. They point out that the proportion of condensed fuel residues present in the lubricant eventually attains an equilibrium in the crankcase of automobile engines. They consequently consider it advisable to make up the original oil to such a composition that it possesses sufficient low boiling products to be at the equilibrium point before it is employed in the engine. By this means the oil will not undergo any considerable change in viscosity whilst in use. The results of extensive tests with oils of this description are given and the results appear to be satisfactory.

The oils marketed under the name of the "Isovis" Oils, which contain volatile constituents so as to make a viscosity equilibrium whilst in the crankcase, are the subject of an article in the *Petroleum Times*, February 5th, 1927. The use of these equilibrium oils, it is pointed out by Kauffman,[9] indicates that it is possible to make it very easy to market recovered lubricants. Hitherto, one of the greatest difficulties in recovering used lubricating oil has been the removal of the small quantity of petrol residues contained in such lubricants. As it is now becoming common practice to make an equilibrium mixture before marketing the oil this should demonstrate

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[5] 927, 123, 665.
[6] March 25, 1927.
[7] *Ind. & Eng. Chem.*, 1926, **18**, 471.
[8] *Ind. & Eng. Chem.*, 1926, **18**, 486.
[9] *Oil and Gas Journal*, February 3, 1927.

the fact that it is not necessary to have a high flash-point in an oil for crankcase lubrication.

Transformer Oil.—The transformer oil specification has recently been revised by the Committee of the British Engineering Standards Association, and in its new version differs very considerably from the specification which has hitherto been in existence. The old specification demanded oils of comparatively high flash-point and permitted a fairly high cold test. Practical experience has indicated that there is no necessity for a high flash-point in transformer oils, whilst several cases of breakdown have occurred where the cause of the trouble has been the freezing of the oil at low temperatures. The original specification was such as to make it extremely difficult to employ Russian base oils on account of the flash-point stipulations and, consequently, the whole of the business has been done in oils of American origin. The new specifications allow for oils of various cold tests, but are comparatively lax on the flash-point, and it is highly probable that the oils used in future will be almost entirely of Russian base, as the Russian oils lend themselves to the manufacture of sludgeless transformer oils, as they require a smaller quantity of acid in the refining process and also the losses due to acid treatment are lower with Russian oils than with oils of American origin.

The change to the new specification is therefore very important, as, although it does not debar American oils from passing through the specification, it will probably result in the almost exclusive use of Russian products as transformer oils in this country.

The composition and recovery of crankcase lubricating oils is the subject of numerous papers, but the information contained in the majority of the newer papers consists mainly of reiteration of facts which have already been stated. Several of the newer processes involve the use of contact clay filtration with or without preliminary acid treatment—in fact, there is a tendency for contact recovery processes to approximate to the treatment applied to the raw distillates in the original preparation of the lubricants from the crude.

A review of the various methods employed in America for the recovery of crankcase lubricants is given by Kauffman.[10]

The use of high-vacuum distillation plant has been greatly extended during recent years and has particular value in the preparation of lubricating distillates from asphaltic base crude. The process has been described in detail by Steinschneider.[11]

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[10] *Oil and Gas J.*, February 10, 1927.
[11] *Journ. Inst. Petr. Tech.*, 1925, p. 514.

The Diesel Engine Users' Association have again prepared a report on the working costs of Diesel engine installations, the present report being for the year 1925-1926.

The number of power stations from which reports have been obtained this year is thirty-seven in this country with a further nine reports from overseas stations. The total number of stations that reported last year and the amount of current generated are somewhat larger than for the previous year. The prices paid for both fuel oil and lubricating oil show only a small change. There has been a slight improvement in the consumption of fuel oil per unit generated and a marked improvement in the consumption of lubricating oil. A considerable number of members of the Diesel Engine Users' Association are now buying lubricating oil to the Association's specification, which calls for a high-grade Pennsylvanian product. The cost of operating the engines per unit generated on the home stations shows a slight improvement, the reduction being from ·806d. per unit for 1924–1925 to ·799d. per unit during the year 1925–1926.

Heavy Distillates, Fuel Oils, Asphalts and Residues.*

By F. H. Garner, Ph.D. (Member).

In the course of the United States Government Fuel Economy survey of its own power plants, a comparison has been made of the various types of oil burner equipment used under power plant boilers. The burners are classified as: (1) those using steam for atomising the oil, and (2) those using mechanical means for this purpose. The comparison is made by J. F. Barkley in Reports of Investigations of the Bureau of Mines, Serial No. 2730. Burners using steam have had the most prominence in this field for a long period. The mechanical atomising type of burner successfully applied on shipboard, however, pointed to a possible betterment in land work. Analyses were made of the products of combustion with various burners in different types of furnaces, and in all the tests the burners were handled by experts and represent the best conditions for the particular arrangement tested. Burners using steam for atomisation were found to give slightly better carbon dioxide figures and lower oxygen without the presence of carbon monoxide. The importance of correct design of combustion space is again emphasised, and it was found that the rule for adjusting

* Paper received May 5, 1927.

burners to secure a slight haze of smoke in the stack may at times be quite wrong, as this smoke haze can be secured with various percentages of carbon dioxide for the same furnace. In making a comparison of the two types of burners, Barkley puts forward the following considerations: "The mechanical natural draft type has the advantage of the steam type by, say, 2 per cent. to 3 per cent. of the total heat in the fuel chargeable to the latter's use of steam for atomising. In order to compensate for this handicap, the steam type must be able to obtain better combustion, so that the loss in the dry flue gases is less than that obtained with the mechanical type. For example, a CO_2 content of 9·6 per cent. gives about 3 per cent. more loss in the dry flue gases than 13 per cent. CO_2. Much effort and study have been put upon the furnace in the use and development of the steam type. The solution of the problem in the development of the mechanical natural draft type, which is at a disadvantage when compared to the forced draft type, is in furnace study rather than concentration on burner arrangements."

The combustion of fuel oils is dealt with by W. Kemp,[1] who gives the products of combustion, combustion chart, fuel loss, volumetric percentage of carbon dioxide at various stack temperatures and humidity table for a fuel oil of the following composition: carbon 84 per cent., hydrogen 11 per cent., oxygen 1·0 per cent., nitrogen 1·0 per cent. and water 0·5 per cent.

Masut.—A considerable amount of work has been reported during the present year on the properties of the residues from Grosny petroleum which contain very large proportions of paraffin wax.

A. Sachanov and N. Wassiljev[2] find that in determining the wax content by Holde's method, a certain quantity of wax is decomposed during the distillation of the masut, and that this introduces errors where the wax content is over 2 per cent. Thus the distilled portion of an oil containing 13·04 per cent. of wax was found to contain only 8·35 per cent. The rate of distillation has a marked influence upon the extent of the decomposition, and as it is very difficult to regulate the rate of distillation this method gives erratic as well as inaccurate results. Direct precipitation by means of alcohol-ether or ethyl-alcohol-amyl alcohol mixtures gives results up to 400 per cent. high owing to the simultaneous precipitation of resinous material. This method, however, gives more accurate results than Holde's method when the wax content is high. These authors recommend the use of amyl

[1] *Oil Eng. Tech.*, 1926, 7, 303. *Chem. Abst.*, 1926, 20, 3561.
[2] *Neftjanoe i slancevoe Chozstvo*, 1925, 8, 44-51. *Chem. Abst.*, 1926, 20, 1318.

alcohol-ethyl alcohol first, and then reprecipitation with ether-alcohol mixture. 10 per cent. of cylinder oil in paraffin wax was found to lower the melting point by 0·9° C., so that melting point of the separated wax is not a satisfactory test for purity.

The separation of paraffin wax from masut has been studied by a number of authors. It is well known that the presence of asphaltic or resinous substances prevents crystallisation of paraffin wax from petroleum products, and thus produces a marked effect on the setting point.

N. Chernoshukov[3] found that the removal of resins from masut of maximum and minimum solidifying points (determined after pre-heating to 60 and 100° C. respectively) raised the solidifying points to 25–27° C. and that this temperature was independent of previous heating. Absorption of resins from a saturated solution of paraffin wax in kerosine was found to increase as the melting point of the wax used increased, and the quantity of resin absorbed at different temperatures depended on the solidifying point of the product. A comparison of various methods of determining the hardening temperature of masut from Grosny and Baku has been made by Holde.[4]

Vaseline from Grosny Petroleum.—The removal of resinous material from technical vaseline prepared from masut has been investigated by Voronov,[5] who found that red clay and silica gel were the most active absorbents. The silica gel can be regenerated by heating several times. Boneblack is found by Walgis[6] to decolorise liquefied masut or masut in petroleum ether very slowly, but by using diatomaceous earth first (1·2 parts) and boneblack second (0·4 part) better results were obtained, giving a colourless vaseline to a yield of about 47 per cent. from the crude. In the removal of asphalts by means of fullers earth containing hydrosilicate H. Herbst[7] finds that silit absorbs 2·5 per cent. of its weight of asphalt. The chemical composition of the resins in masut has been examined by P. Smirnov,[8] who gives the iodine numbers, sulphur, and molecular weights of resins absorbed by boneblack and redissolved by various solvents.

Sachanov[9] has determined the asphaltene content of various residues from Grosny petroleum, and finds that the asphaltenes derived from blown asphalts were similar in properties to those

[3] *Neftjanoe i slancevoe Choztvo*, 1925, **8**, 640. *Chem. Abst.*, 1926, **20**, 3075.
[4] *Neftjanoe i slancevoe Choztvo*, 1925, **8**, 786. *Chem. Abst.*, 1926, **20**, 1743.
[5] *Neftjanoe i slancevoe Choztvo*. 1925, **8**, 779. *Chem. Abst.*, 1926, **20**, 2743.
[6] *Neftjanoe i slancevoe Choztvo*, 1925, **8**, 784. *Chem. Abst.*, 1926, **20**, 2743.
[7] *Neftjanoe i slancevoe Choztvo*, 1925, **8**, 286. *Chem. Abst.*, 1926, **20**, 1902.
[8] *Neftjanoe i slancevoe Choztvo*, 1925, **8**, 933. *Chem. Abst.*, 1926, **20**, 986.
[9] *Petroleum Zeit.*, 1926, **22**, 424.

obtained from steam refined asphalts. He finds that asphaltenes are lyophylic colloids in aromatic and similar hydrocarbons and petroleum tar, but lyophobic in paraffins and naphthenes. In Russian petroleum where lyophobic constituents predominate, the asphaltenes are mostly in the disperse state, but Californian and Mexican petroleum contain a high proportion of tar which is lyophylic to asphaltenes.

F. Lavirotte[10] obtains petrolatum from petroleum residues and heavy oils by treatment with sulphuric acid at elevated temperatures and subsequent neutralisation by means of porous clay and calcium carbonate.

The following provisional standards for Russian petroleum fuels are given by V. Viliashnikov.[11]

Grade.	Flash point.	Freezing point.	For Grosny Oils Flash point.	For Grosny Oils Freezing point.
A ..	Over 60° C. ..	Below −10° C. ..	Over 50° C.	Below −5° C.
B ..	„ 60° C. ..	−10° C. to 8° C. ..	„ 50° C.	−5° C. to 8° C.
C ..	„ 60° C. ..	8° C. „ 24° C. ..	„ 50° C.	„
D ..	„ 60° C. ..	24° C. „ 35° C. ..	„ 50° C.	„

Mineral acids or alkalies must not exceed 0·1 per cent., solid incombustible material must be below 0·5 per cent., and viscosity Engler at 50° C. for all grades should not exceed 7°.

For ship masut, the following specification is proposed: density 15° C. 0·890–0·920, flash point over 100° C., maximum sulphur 0·2 per cent., maximum viscosity 6° (Engler 50° C.) and solidifying point below −5° C.

Bituminous emulsions.—In view of the wide demand for bituminous emulsions, where it is desired to use solid asphalts in liquid form for cold applications such as in road making, manufacture of briquettes, impregnation of concrete, and the manufacture of roofing felt, it is of interest to note that a very large number of patents have been taken out covering the use of various types of emulsifying agents.

F. Levy[12] uses up to 10 per cent. of emulsifying agent containing tannic acid and dilute aqueous alkali. The oxidation products from paraffin wax are described for this purpose by the Bataafsche Pet Maatschappig.[13] In this case the paraffin is oxidised with or without the presence of catalysts (fatty acid, salts of cobalt, manganese lead, etc.) and a dilute aqueous solution of alkali is used in the manufacture of the emulsion.

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[10] E.P. 240,803.
[11] *Neftjanoe i slancevoe Chozivo*, 1925, **8**, 939. *Chem. Abst.*, 1926, **20**, 2743.
[12] Can. P. 262,783.
[13] Dutch P. 14,751.

G. S. Hay[14] used 10 per cent. of gum, and in U.S. Patent 1,582,467, caustic potash solution and potato starch or similar product.

The use of sulphonated fatty oils is covered by H. H. Mackay in British Patent 236,641, and of cholesterol oleic acid and caustic soda in British Patent 233,430.

Partly coagulated casein, starch, egg, albumin, or Irish moss, is protected by L. C. Lutjens and R. O. Child in British Patent 238,586.

An interesting process by L. Kirschbraun[15] describes the use of colloidal clay and a flocculating agent such as aluminium sulphate or sodium acid phosphate.

Rubber latex (5–20 per cent. by weight) is used as an additional agent where oleic acid and caustic soda are employed, by F. Levy, British Patent 254,004.

The determination of asphaltenes in dark mineral oils by the following method is found by D. Holde[16] to give consistent results: Precipitation with light petroleum, solution of asphaltenes in benzene, and evaporation of the benzene is followed by extraction with absolute alcohol to remove paraffin wax. The residual asphaltenes are again precipitated with petroleum ether and the above procedure repeated until the redissolved precipitate shows no traces of paraffin wax.

The production of cresylic acids from petroleum cracked distillates is described by L. J. Catlin,[17] 0·007 per cent. of phenols were obtained by extraction with caustic soda solution. The purified phenol fraction distilled mainly between 195 and 227° C., but contained no cresols, although it gave tests for cresylic acid.

In view of the comparatively large proportion of vanadium in the ash of some crude petroleums it is of interest to note that the extraction of vanadium from petroleum still residues and ash is described by Oberle in U.S. Patent 1,570,170 and by Baldeschwieler, U.S. Patent 1,563,061.

A new method of preparing blown asphalts by spraying oil into a heated chamber in which the proportion of oxygen present is regulated to prevent ignition or substantial vaporisation, is described by J. S. Miller in U.S. Patent 1,586,376.

A criticism of the Kraemer-Sarnow method of determining the melting point of asphalt is made by J. Lagervist and

[14] B.P. 239,120 and 254,012.
[15] U.S.P. 1,567,061.
[16] *Petroleum*, 1926, **22**, 799.
[17] *Ind. Eng. Chem.*, 1926, **18**, 743.

M. Fredman[18] who point out that slight changes in the experimental conditions lead to discrepant results.

The naphthenic acids from gas oil derived from Californian crude petroleum have been examined by V. Tanaka and S. Nagai[19] and were found to be intermediate in specific gravity to similar acids isolated from two Japanese crudes. These authors state that there are two series of naphthenic acids having isomeric composition and which are differentiated chiefly by the specific gravity.

[18] *J.S.C.I.*, 1926, B 261.
[19] *J.S.C.I.* (*Japan*), 1926, **29**, 1-7.

Special Products.*

By W. J. Wilson, F.I.C., A.C.G.I. (Member).

Paraffin Wax.

J. A. Carpenter[1] has obtained by fractionation of wax from Burmah crude oil a large number of hydrocarbons ranging from $C_{21}H_{44}$ to $C_{34}H_{70}$, including some isomers. A paraffin of melting point 96·5° C., probably $C_{57}H_{116}$, was isolated from sucker rod paraffin. A study of the crystallisation of paraffin wax revealed the existence of a definite transition point between two crystalline forms. The phenomena associated with the presence of air and of oil in paraffin are discussed, and a method of analysis of oil-wax mixtures given.

A. Sachanov and M. Bestuschev[2] separated paraffin from petroleum without distillation, studied their solubilities, and found no difference between them and the corresponding distilled paraffins.

F. W. Padgett, D. G. Hefley and A. Henriksen[3] studied the crystallisation of paraffin microscopically, and found that different types of crystallisation are dependent upon the nature of the wax and its associated substances.

Determination of the boiling points of paraffins isolated from Scottish paraffin wax (F. Francis and N. E. Wood)[4] showed the compounds to be identical with synthetic normal paraffins.

* Paper received May 7th, 1927.

[1] *Journ. Inst. Petr. Techn.*, **12**, 288.
[2] *Petroleum Z.*, **22**, 484.
[3] *Ind. Eng. Chem.*, **18**, 832.
[4] *J. Chem. Soc.*, 1926, p. 1420.

Oxidation Products.

F. Francis and H. F. Gauntlett[5] have investigated the nature of the substances, other than acids, which are formed by the oxidation of paraffin by atmospheric oxygen. No primary alcohols were detected, but dihydroxy alcohols, hydroxy-ketones and diketones are probably present and the presence of secondary alcohols and ketones was definitely proved, corresponding in composition with that of the normal hydrocarbons which constituted the paraffin.

G. S. Petrov, A. I. Danilovich and A. Rabinovich[6] obtain acidic products by oxidation of oils.

J. Marcusson and W. Bauerschäfer[7] isolated acids formed by oxidation of transformer oil.

Patented oxidation processes include the production of aldehydes and acids by oxidation of gaseous paraffins with air (C. P. Byrnes).[8]

Insecticides.

Petroleum products find a gradually increasing use as insecticides. W. W. Yothers and J. R. Winston[9] use colloidal clays in lieu of soap for emulsification of oils with satisfactory results. E. R. de Ong[10] discusses the properties which oils used for insecticidal sprays are required to possess, and A. L. Melander, A. Spuler and E. L. Green have investigated the most suitable oil fraction for the purpose.[11] G. P. Gray and E. R. de Ong[12] find that the toxicity of oils towards vegetation is roughly proportional to the content of unsaturated compounds in the oils. A general paper on petroleum insecticides is published by W. W. Yothers, A. J. Ackerman, L. Haseman and J. J. Davis.[13]

The California Spray Chemical Co.[14] states that the phytocidal properties of petroleum oils are due mainly to unsaturated hydrocarbons, sulphur, the lighter cyclic hydrocarbons and organic acids. For insecticidal purposes, therefore, highly purified oils are required if phytocidal effects are to be avoided.

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[5] *J. Chem. Soc.*, 1926, p. 2377.
[6] *Trans. Karpov Inst. Chem.*, 1925, (4), 143. *Seifensieder-Zeit.* **53**, 297, 475, 494.
[7] *Chem. Zeit.* **50**, 263.
[8] U.S.P. 1,588,836.
[9] *J. Agr. Research* **31**, 59.
[10] *Oil Gas J.* **24**, (36), 142.
[11] *Agr. Exp. Sta.* (*Washington*) *Bull.* 197.
[12] *Ind. Eng. Chem.* **18**, 175.
[13] *J. Econ. Entomol.* **19**, 407.
[14] B.P. 245,179.

Naphthenic Acids.

Y. Tanaka and S. Nagai[15] have issued a number of papers in continuation of their work on naphthenic acids, and have isolated a number of these acids from petroleum distillates from various sources. The acids derived directly from petroleum are shown to be identical with those obtained from the waste lye produced in the refining of the same oil.

M. Naphthali[16] and G. L. Stadnikov and A. A. Dondé[17] attempted to obtain ketones from naphthenic acids, but the results were negative. J. Mikumo[18] compares the properties of naphthenic soaps with other soaps, and a similar study is made by Y. Kawakami.[19] The properties and uses of the acids are discussed by F. Zernik,[20] who also proposes the use of naphthenates for production of artificial resin compositions.[21]

Miscellaneous.

An excellent review of the processes of preparation of alcohols from unsaturated hydrocarbons is contributed by B. T. Brooks.[22] Another paper on this subject is by S. D. Kirkpatrick.[23] H. S. Davis and W. J. Murray[24] contribute a paper on the properties of tertiary alcohols, and discuss their possible uses as solvents, and for preparation of synthetic products. P. I. Schestakov[25] obtains sulphonic acids by treating mineral oils with sulphuric acid, separating the tar, and heating the oil with aqueous acetic acid or one of its esters.

Standard Development Co. recover vanadium from petroleum ash by treatment of the latter with a solution of caustic soda.[26] A. Oberle[27] leaches petroleum residues, free from volatile matter, with water and steam.

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[15] *J. Faculty Sci. Imp. Uni. Tokyo* **16**, 171, 183. *J. Soc. Chem. Ind.* (*Japan* **29**, 1, 58, 115.
[16] *Chem. Umschau Fette, Oele, Wachse Harze* **33**, 1.
[17] *Trans. Karpov Inst. Chem.* **4**, 188.
[18] *J. Soc. Chem. Ind.* (*Japan*) **28**, 1121.
[19] *J. Soc. Chem. Ind.* (*Japan*) **29**, 64.
[20] *Erdöl Teer* **1**. *Chem. Zentr.* **96**, ii., 1403.
[21] U.S.P. 1,537,572.
[22] *Chem. Reviews* **2**, 369.
[23] *Chem. Met. Eng.* **33**, 402.
[24] *Ind. Eng. Chem.* **18**, 844.
[25] B.P. 247,940.
[26] U.S.P. 1,563,061.
[27] U.S.P. 1,570,170.

Analysis and Testing of Petroleum.*

By J. S. Jackson, B.Sc., A.I.C. (Member).

The peculiar difficulties encountered in the testing of petroleum products are such that the development of accurate and convenient tests necessarily proceeds at a very slow rate. It can, however, be said with some confidence that satisfactory, if not spectacular, progress has been made during 1926.

The actual number of acceptable new tests put forward has not been very great, and this may have been due to the success which has attended the efforts of the various technical bodies to standardise testing methods. Thus, while many of the standardised methods may be far from perfect, they have proved exceedingly useful in maintaining some measure of uniformity, and stemming the harassing and confusing stream of individual efforts to solve the many difficulties which the petroleum chemist has to face.

In this connection it is of interest to note that the standard methods drawn up by the Institution of Petroleum Technologists are being completely revised, amplified and brought up to date, and a new volume which should be even more valuable than its predecessor should be available in the near future.

In spite of the efforts of many workers throughout the "Petroleum" world, many difficulties still remain and many problems still await solution. For instance, the chemist has to admit that he is still unable to determine with any degree of accuracy the composition of petroleum spirits. No real progress has been made in the matter, and the present position is particularly unsatisfactory in view of the great variety of gasolines now upon the market.

It is to be hoped, therefore, that the urgent need of a reliable method for evaluating all the various cracked and blended spirits will stimulate the efforts of petroleum chemists and lead to the working out of satisfactory schemes of examination.

The A.S.T.M. D86-26T Method for the distillation of gasoline appears to have reached a stable condition, but it is now being realised that while it affords a simple and accurate method for testing gasoline from a commercial point of view, it does not necessarily foretell accurately how a given gasoline will behave in a carburettor.

Thus, a demand has arisen for a means of measuring the volatility of a fuel under conditions similar to those obtaining in an

* Paper received May 1, 1927.

internal combustion engine. A very satisfactory test of this type has been described by T. S. Sligh.[1]

In this test air and fuel are delivered at measured rates to a heating coil maintained at any desired temperature. The volumes of spirit evaporated at various temperatures can be measured, and an equilibrium distillation curve constructed.

An Equilibrium Boiling Point Method was described by W. A. Whatmough.[2]

The lack of a satisfactory method for estimating and comparing the burning qualities of kerosine is still felt. Some progress has, however, been made by comparing the heights to which the flame obtained with a small circular wick may be raised without the formation of smoke. Such a wick can easily be trimmed, and the shape and type of flame are practically independent of slight variations in the condition of the wick. The flame must naturally be protected from draughts by a suitable casing, so that the height of the flame can be accurately measured by means of a lens fitted with a scale.

An important advance was made in 1926 when the Board of Trade, in conjunction with the Institution of Petroleum Technologists and various other experts, modernised and specified more closely and accurately the Abel Flash Point Tester.

Interesting and valuable work upon the application of the Critical Solution Temperature Test to the study of the chemical composition of kerosines was published by J. A. Carpenter.[3]

Considerable attention has been given to the testing of lubricating oils, and a great deal of important though unpublished work has been done. The A.S.T.M. Pour Test, though still widely used is not considered entirely satisfactory, and the tendency has been to utilise methods in which the sample of lubricating oil is contained in a U tube of specified dimensions and cooled under specified conditions. The fluidity of the oil is tested by applying a predetermined air pressure to one limb of the tube, the oil being considered set when no movement can be detected.

Considerable progress has been made in viscometry, and a very convenient and accurate viscometer has been developed and described by Dr. Vogel.[4] By means of this viscometer viscosities in absolute units can be rapidly and accurately determined, and the results can be readily converted in terms of the Redwood Engler or Saybolt instruments. Dr. Vogel's viscometer is also constructed so that viscosity determinations may readily be made

[1] *Oil and Gas J.*, Aug., 1926, p. 72.
[2] *Ind. Eng. Chem.*, 1926, **18**, 4345.
[3] *Journ. Inst. Petr. Techn.*, 1926, **12**.
[4] D.R.P. No. 37,339. *Petr. Zeit.*, Oct., 1922, **35**, 561.

under pressure upon highly viscous oils. This is a very important feature, since it facilitates the exploration of the viscosity curves of lubricating oils at low temperatures.

Attention has been given to the determination of traces of water in mineral oils, and an interesting method was described by W. Boller.[5] This method depends upon the formation of acetylene from purified calcium carbide under carefully controlled conditions. The percentage of water is ultimately calculated from the percentage of copper obtained either gravimetrically or volumetrically from the precipitated cuprous acetylide.

Many workers have been engaged during 1926 in studying the oxidation of lubricating oils, but some time must yet elapse before an acceptable standard oxidation test is likely to emerge. The results published by Harold Moore and James Barrett[6] serve to indicate the general trend of the work already undertaken.

The standard methods for the examination of transformer oils have been reconsidered and revised, and it will be seen that considerable advances have been made particularly in connection with the sludging test.

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[5] *Chem. Zeit.*, 1926, 437.
[6] *Journ. Inst. Petr. Techn.*, 1926, 12.

Synthetic Fuels.*

By Alfred W. Nash, M.Sc., F.C.S., M.I.Mech.E. (Member), and Oliver C. Elvins, M.Sc., A.I.C. (Associate Member).

The preceding year has witnessed a considerable advance in our knowledge of the possibilities of finding liquid fuel substitutes, and a committee appointed by the Ministry of Agriculture and Fisheries (Power Alcohol Production, 1926, H.M. Stationery Office) concluded that the most likely processes were: the production of alcohol from wood or from water-gas, and the two much-discussed methods of treating coal, viz., the Bergius process and the low-temperature carbonisation method.

As the particular processes which utilise water-gas or gas mixtures containing carbon monoxide and hydrogen are synthetic and the others mentioned involve the degradation of large molecules, it will be necessary to consider the water-gas process only in the sequel.

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* Paper received April 1, 1927.

The manufacture of methyl alcohol from carbon monoxide and hydrogen has been carried out by the B.A.S.F., which firm has covered the process by a large number of patents which incidentally include a bewildering number of combinations of metals and oxides for use as catalysts. The shortcomings of methyl alcohol as a petrol substitute do not need recapitulation, but the passage of hydrogen and carbon monoxide under pressure over a heated catalyst can be made to give rise to products of a more suitable nature from the fuel point of view, for instance, higher alcohols, ketones and ethers have been recorded as products. A recent patent by the B.A.S.F.[1] describes the use of iron in catalyst mixtures, which is of interest in that they had hitherto eschewed the use of this metal.

They state that a catalyst containing free iron, cobalt or nickel induces the formation of methane, water and carbon, and "Example 5" states that the addition of iron oxide to a methanol-forming catalyst composed of zinc oxide and chromium oxide causes the formation of hydrocarbons with a heavy deposition of carbon. If, however, sulphur be added to combine with the free iron formed by reduction, then at 400° C. and 200 atm. pressure carbon monoxide and hydrogen are converted into methyl alcohol and higher molecular compounds. The hydrogen of this gas mixture can be substituted by steam or hydrocarbons, it is claimed. No information is vouchsafed concerning the relative amounts of alcohols other than methyl formed, but it seems that to produce these homologues the temperature of reaction must be higher and the gas speed slower, which presumably is conducive to deleterious carbon deposition on the catalyst. A long article by Patart on the pressure method of treating water-gas[2] gives an account of the economics of the process and shows the difficulties raised by the accumulation of the comparatively inert gases nitrogen and methane in the circulating system. The interesting statement is made that he obtained a product which contained 10 to 12 per cent. of isobutyl alcohol, separable by fractional distillation from the methyl alcohol, and less volatile products which were formed simultaneously. The proportion of isobutyric acid in the product could also be increased by using a suitable catalyst, details of which are not given.

This appears to be a distinct advance in the direction of finding a catalyst which will give a preponderating amount of a homologue of methyl alcohol instead of a mixture from which no one substance (except in the case of methyl alcohol) can be easily separated.

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[1] E.P. 254,760.
[2] *Chim. et Ind.*, 1926, **16**, 713.

Patart inclines to the view that liquid products made by this process cannot compete commercially with petroleum distillates as fuels, and that it is more likely that they will be utilised in chemical industry. For instance, isobutyl and amyl alcohols would find a ready market as solvents, and the organic acids could be absorbed in the cellulose industry or be converted into the corresponding ketones. There is, of course, the possibility that suitable alcohols could occupy a position similar to that of benzole, which is partly used as a fuel in conjunction with petrol and partly as a raw material in chemical industry.

As some support for Patart's view that the process will be directed towards the formation of useful raw chemical materials rather than fuels, it should be pointed out that the majority of patent applications are concerned with the production of methyl alcohol rather than hydrocarbons, which are cited as by-products in certain circumstances.[3] The former patent (E.P. 262,364) describes the formation of keten by passing the gas mixture required by the equation $3CO+H_2=CO_2+CH_2=C=O$ over granular zinc oxide at 260–270° C. under a pressure of 120 atm.

Other patents indicate the popularity of the synthetic methyl alcohol process, *e.g.*, Woodruff and Bloomfield,[4] cover the use of ferric hydroxide and magnesium hydroxide, and ferric hydroxide and zinc oxide as catalysts, while Casale[5] gives a list of seven possible simple reactions.

A résumé of the various substances which have actually been isolated from the products of the pressure process is given by Mittasch[6].

A method discovered by Fischer and Tropsch[7] renders it possible to convert mixtures of carbon monoxide and hydrogen into what is essentially a mixture of hydrocarbons. The process is carried out by passing the two gases at atmospheric pressure over a catalyst heated to about 270° C. The catalyst should contain the oxides of iron, cobalt or nickel mixed with copper or with a non-reducible oxide such as chromium oxide and before use the mixture is reduced by hydrogen at about 350° C. Iron or cobalt is the basic ingredient of the catalyst mixtures cited by Fischer and Tropsch, and the range of possible catalysts does not seem to be so extensive as in the pressure process where such materials as basic zinc chromate (Patart) or lower oxides (Audibert) have been used successfully to accelerate the formation of methyl alcohol.

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[3] *Cf.* Dreyfus, E.P. 262,364 and 262,494, and 262,832 of 1925.
[4] U.S.P. 1,609,593 and 1,608,643, of 1926.
[5] E.P. 252,573 of 1926.
[6] *Ber.*, 1926, **59**, 13-36.
[7] *Brenn. Chem.*, 1926, **7**, 97; *Ber.*, 1926, **59**, 830, 832.

An important feature of the reaction lies in the fact that suitable modification of the catalyst leads to the formation of a preponderance of products with a desired distillation range. For instance, iron and zinc oxide as a catalyst accelerated the conversion of carbon monoxide and hydrogen into gaseous hydrocarbons, while a mixture of cobalt and chromium oxides gave liquid and solid hydrocarbons as well as gaseous. A considerable amount of liquid products formed are carried away by the effluent gas and it is necessary at present to use such means as active charcoal or low temperatures for their recovery. The oxygen of the carbon monoxide is removed as water or carbon dioxide or both, according to the catalyst used.

Fischer and Tropsch showed that ethane, propane and butane, with minimal amounts of ethylene, propylene and butylene, constituted the hydrocarbon fraction of the escaping gases. A benzine fraction was obtained with a boiling range of about 20° C. to 180° C., and a petroleum-like fraction distilled between 180° and 330° C.

By using an iron-copper-alkali catalyst they obtained a quantity of solid hydrocarbons sparingly soluble in acetone, from which solvent crystallised a colourless odourless paraffin with a solidification point of 61° C. The formation of substances with a boiling point higher than the reaction temperature is a disadvantage, in that these tend to accumulate on the surface of the catalyst and consequently act as slow poisons, which presumably is one reason why the pressure process is not conducted with a view to hydrocarbon formation. Regeneration of the catalyst could be performed by steaming, or by roasting in a current of air, followed by reduction with hydrogen.

It is seen that the practical side of the interaction of carbon monoxide and hydrogen has developed with extraordinary rapidity; unfortunately the same statement cannot be truthfully made concerning the theoretical side.

If a good *ad hoc* hypothesis could be formulated to account for the diversity of products obtainable by varying the pressure, temperature, rate of gas flow and the catalyst, then results of incalculable value would follow rapidly in technology. Fischer and Tropsch[9] have advanced the view that hypothetical high-carbon carbides are formed as intermediate products, these being then reduced by the hydrogen of the reactants to form hydrocarbons.

This statement was criticised by the authors on the ground that oxygen containing organic compounds are found in the

[9] *Loc. cit.*

products,[9] but Fischer and Tropsch[10] consider that the formation of hypothetical oxycarbides from the non-reducible oxides used as catalysts remove this difficulty. The suggestion is ingenious, but it seems more likely that intermediate substances of a carbonyl nature are formed; direct experimental evidence is still very scanty, and more investigation of simpler catalytic reactions is necessary before a feasible explanation can be advanced to account for all the phenomena encountered in the catalytic interaction of carbon monoxide and hydrogen.

In conclusion it can be said that the pressure process for methyl alcohol is a commercial success, that it can be modified to yield liquids suitable for use as fuels, but evidence is not yet forthcoming that such modifications will be an economic success. Hydrocarbon formation at atmospheric pressure holds much promise for the future of synthetic petrol, but investigation is required on fairly large scale apparatus before any reliable statements can be made concerning the likelihood of its adoption as a commercial proposition.

[9] Elvins and Nash, *Nature*, 1926, **118**, 154.
[10] *Brenn. Chem.*, 1926, **7**, 299.

Oil Engines.*

By J. F. Alcock, B.A. (Cantab.).

The past year has been marked by no outstanding innovations, but it has seen a steady development which is largely the fruit of the painstaking research of the last few years. The progress may be gauged by the facts that 400,000 B.H.P. of Diesel engines were installed last year for ship propulsion alone, and that of the mercantile tonnage now under construction more than half is Diesel driven.

The chief feature of the year is without doubt the construction of high-powered engines, mostly for passenger liners. This has been rendered possible, partly by a better knowledge of the thermal and mechanical problems that beset the large cylinder, and partly by the use of double-acting cylinders. This latter development has been imminent for some time, since the orthodox single-acting crosshead engine is, structurally, a double-acting engine minus its lower cylinder cover and accessories. By adding these the power output can be nearly doubled with a relatively small increase in weight and cost. That it has not been done before is due to the

* Paper received April 30, 1927.

difficulty of obtaining efficient injection in a combustion chamber divided by the piston rod, and to that of cooling the rod. Both these problems now appear, however, to have been solved with a fair degree of satisfaction.

The largest engine built during the year was the 15,000 B.H.P. M.A.N. engine installed at Hamburg for electricity supply. This has nine double-acting two-stroke cylinders. For ship propulsion the largest units were the 7500 B.H.P. engines of the "Asturias" and "Alcantara." These are of the Burmeister and Wain double-acting four-cycle type, built by Harland and Wolff, with eight cylinders. Of single-acting engines, the largest were the Sulzer 5800 B.H.P. engine, and the Doxford opposed piston unit of 5500 I.H.P.

The performance of these engines leaves little doubt that the Diesel engine of 10,000–15,000 B.H.P. is a practical proposition, and for the vast majority of the world's shipping such powers are ample. Whether the use of these enormous slow-speed engines is the best method of obtaining large outputs is not so certain. The internal combustion engine is at its best with relatively small cylinders running at a fairly high speed. With large low-speed units the weight and cost per H.P., the main drawbacks of the Diesel engine, are apt to be excessive, while with such large cylinders the heat flow and thermal stresses must be such as to leave little margin of safety.

An alternative method is the use of a number of relatively small high speed engines. If used for electricity generation their output can, of course, be combined without difficulty, but in marine work the problem is not so simple. Electrical transmission is, in most cases, too costly, but mechancial gearing appears to be fairly satisfactory, within limits. This scheme was first employed as a means of utilising surplus submarine engines in commercial vessels, but its advantages as regards cost and weight have led to its continuance. In some cases the engines are directly coupled to the gearing, but in others a hydraulic clutch and reverse gear is interposed. This protects the gears from the irregularities of the engine torque, and also facilitates manœuvring, since the engine itself need not be stopped or reversed.

If, as seems probable, the economic limit of cylinder size has been reached or passed, there should be a good future for such schemes of this kind.

High-Speed Engines.

At the other end of the scale, a determined attempt is being made to produce a small and light high speed engine for work such as lorry driving. In Germany and the U.S.A. several small engines have been constructed for this purpose, giving outputs of about

10—20 B.H.P. per cylinder at speeds up to 1300 r.p.m. So far, however, their performance does not seem to compare favourably with that of the corresponding petrol engine.

Contrary to expectation, high engine speed does not of itself appear to give rise to difficulties with injection and combustion, but with these very small cylinders starting is difficult, and the injection orifices, owing to their small size, give trouble through choking with grit and through erosion.

It is open to doubt whether the Diesel engine is really suited to this class of work. Apart from the need for expensive fuel, the petrol engine is a very satisfactory unit, and in most cases the fuel bill is not the chief item in the running costs. With the unskilled handling that this type of engine usually receives, the Diesel is not likely to be so reliable as the petrol engine, while the smell of its exhaust would be a serious drawback, especially for motorbus work. It is almost certain that the authorities would, on this account, prohibit their use in large towns.

The real scope for the high-speed Diesel appears to be in slightly larger powers, say from 100–500 B.H.P. For such outputs petrol is too costly, while in most cases the bulk and first cost of the orthodox Diesel is a serious drawback. There exists it is true, a class of so called "high speed" engines running at 250–400 r.p.m., and used mainly for ships' auxiliaries, but for many purposes these do not go far enough.

For a really high speed Diesel engine of light weight many uses could be found, as in small vessels, electrical plants and locomotive work. This latter is an excellent field for the Diesel engine, owing to the low efficiency of the steam locomotive, but space is severely limited, and the orthodox Diesel is far too bulky. Several Diesel locomotives are being developed on the Continent, but so far with doubtful success. In the less ambitious sphere of rail car propulsion, the Diesel has made good, of particular interest being the use of the Beardmore and Maybach high-speed engines in this service.

There seems reason to anticipate a considerable development of this type of engine. The cylinders are large enough to avoid the starting and injection troubles of the ultra-small Diesel, yet not so large as to render useless the very valuable experience in high speed work gained in the development of the aero engine. The excessive weight and cost of the Diesel engine are its chief drawbacks, and the high speed engine, by reducing these, can open up many new fields of application. For marine auxiliaries and electrical generation generally, they should show to advantage, since their high speed reduces the cost, not only of the engines themselves, but

of the generators they drive. It is mainly due to the high cost of the present medium speed plant that steam auxiliaries are still in demand, in spite of their high fuel consumption.

Two-Stroke Engines.

Though not yet in the majority, the two-stroke engine is gaining ground, especially in the larger sizes. Thus the two-cycle engines constructed during the year (for ship propulsion) numbered only about half the four-cycle engines, but their aggregate output was nearly 80 per cent. of the four-stroke output.

This development is mainly due to the use of independent centrifugal scavenge blowers in place of reciprocating pumps, which are cumbrous and costly. Generally the scavenge blower is driven electrically at a speed of about 2500–3000 r.p.m., power being supplied by auxiliary Diesel driven generators. This high speed is necessary in order to attain the required delivery pressure, but it renders the design of the driving motors rather difficult. In fact, there is, at present, only one maker who will supply them.

Though this system has many advantages over the reciprocating scavenge pump, it is by no means ideal. Owing to the cost of the auxiliary engine, etc., and to the low efficiency of small centrigfual blowers, it is only practicable for fairly large engines. Further the generator and motor act merely as step-up gearing, and one is tempted to ask whether mechanical gearing would not do the same work as effectively and at much less cost.

An alternative method would be the use of a rotary blower of the Roots or the eccentric vane type, coupled direct to an auxiliary engine of high or medium speed, or perhaps geared up from the main engine crankshaft in smaller sizes. These rotary blowers have come to the fore recently as superchargers for motor-car or aero engines, and there seems no reason why they should not be utilised in larger sizes for Diesel engines.

The position of scavenge and exhaust ports has received a good deal of attention lately, and several novel arrangements have appeared, particularly in connexion with double-acting engines.

Fuel Injection.

The airless, or solid injection system appears to be steadily gaining ground. In the earlier solid injection engines it was found necessary, in order to obtain a performance approaching that of the air injection engine, to use extremely high injection pressures, and a number of very small injection orifices, The fuel was stored under pressure in some kind of elastic receiver, and released by the mechanically controlled lifting of the fuel valve. Under these

conditions trouble often occurred with leakage under the very high pressures, and with choking and erosion of the fine injection orifices. Further, it is no easy matter to impart to the fuel valve spindle the very small lift required with the necessary degree of accuracy.

Owing to these drawbacks there was, on the whole, little to choose between the air injection and the solid injection systems as regards mechanical convenience. Recently however, it has been realised that the chief virtue of air injection, the turbulence caused by the incoming blast air, may be obtained by other means, thus giving the performance of the air injection engine with relatively simple injection gear. The present tendency is towards the use of the "jerk pump" system, using a fuel pump which delivers only during the injection period, and a fuel valve operated automatically by the injection pressure. The injection pressures are not as a rule, very high, and only occur during the actual injection period, while the orifices are relatively few and large.

Without turbulence the admixture of the fuel and air would be very poor, but with it excellent results can be obtained. The best systems appear to be those, such as the Hesselman system, in which the air charge is given a definite rotational swirl across which the fuel is injected.

Two-stage combustion continues to be popular in the smaller sizes. In this the fuel is injected into a small auxiliary combustion chamber where part of it burns and the expansion of the air therein drives the rest of the fuel into the main combustion chamber. This system gives as a rule, fairly effective combustion, but the heat losses are high, and it is not easy to control the rate of combustion so as to avoid rough running due to an over-rapid pressure rise.

With air injection systems there is little change to record, beyond the evolution of a number of fuel valves, notably of the Mirrlees and Tosi type, which eliminate the troublesome packing gland on the fuel valve spindle. The steeple type of compressor is gradually being replaced by the differential and radial types, with their more uniform torque.

An interesting air injection engine is the "Hindlmeier." In this blast air is supplied by an independent single stage compressor for each cylinder, the fuel injection valve acting as the compressor delivery valve.

Supercharging.

The use of this is steadily extending. Naturally, in view of the many unknown factors involved, development is proceeding cautiously, and so far the degree of supercharge used is slight,

rarely exceeding 20 per cent. Moreover it is, as a rule, only used to meet temporary overloads, and not employed continuously. Usually the supercharger is of the centrifugal type driven electrically, a system which has in this service the same drawbacks as it has in the scavenging of two-strokes. The driving motor problem is, in fact, worse, since higher pressures are needed, and therefore higher blower speeds. Occasionally steam turbo-blowers are used, which are simple and reliable, but wasteful of fuel, unless exhaust heat is utilised.

Here again there appears to be scope for the rotary displacement blower.

In two ships turbo-superchargers have been installed, driven by the main engine exhaust. As yet, however, no details of their performance is available. Thanks to recent progress in metallurgy, the construction of blading, etc., to stand the exhaust temperature should not be very difficult, since Diesel exhaust temperatures are not very high. It remains to be seen though, how the turbine will appreciate the soot and tar that comes its way when combustion is not quite perfect.

As to the effect of supercharging upon the working condition in the engine cylinder, the evidence is as yet far from complete. It seems certain, however, that the thermal efficiency is practically unaltered, and that the pressures and heat-flow, though greater, are not seriously increased. If this is so, supercharging should be of great value, since it increases the output from a given size of engine, and thus mitigates the main drawbacks of the Diesel, its weight, bulk, and cost. It is, unlikely, though, that it will be much used for very large engines, since in these the heat flow is too large in any case to permit of any appreciable increase.

Hot-Bulb Engines.

For some years the majority of these engines have been changing, by a process of gradual evolution, into the true Diesel type. Step by step the "hot-bulb" has generated into a "hot-spot" and in many cases has altogether disappeared, the compression ratio being raised so as to take over the full duty of providing heat for ignition. In most cases heat is still applied when starting, by means of an electrically heated plug, or in some cases by the combustion of a "slow-match" which is lit by hand and inserted in the cylinder. These expedients will in time probably disappear, in favour of a compression ratio high enough to ensure cold starting.

This tendency has continued during the past year. Apart from this the type has altered little, crankcase compression, with its

attendant drawbacks of low output and poor lubrication, being still universal, though lubrication troubles have certainly been mitigated by improved detail design.

For stationary work the four-cycle cold starting type appears to be encroaching on the market of the two-stroke.

Oil and Gas Developments in Canada.[1]

By G. S. Hume, Geological Survey of Canada.

As outlined in this Journal in a previous article[2] there were two producing oil fields in Alberta at the end of the year 1925. These were the Turner Valley field in the foothills, 35 miles south-west of Calgary, and the Wainwright field in eastern-central Alberta, 120 miles south-east of Edmonton. During 1926 both of these fields have continued to produce oil, and the production in Turner Valley has increased from 169,432 barrels[3] in 1925 to more than 205,000 barrels in 1926. This increase in Turner Valley is due to a larger production from Royalite No. 4 well and to the drilling of several new wells. The production of Royalite No. 4 well has now increased to more than 600 barrels a day of 72 to 73° Baumé naphtha, and, as explained in last year's article, this naphtha is extracted by Smith Separators from a flow of gas of from 17 to 20 million cu. ft. per diem. During 1926 three other wells—Vulcan No. 1, Illinois-Alberta and McLeod No. 2, were drilled into the dolomite, which is productive in Royalite No. 4 well at 3740 ft. At the end of 1926 McLeod No. 2 was still being deepened but had obtained a large volume of naphtha-bearing gas. The drilling of these wells has demonstrated that the main anticlinal structure of Turner Valley is divided into an east and a west anticline separated by a very sharp and deep syncline. The Vulcan well was drilled in the central syncline, and production was obtained at a depth of slightly more than 5000 ft. from the dolomite, which is presumed to be of late Palæozoic age. The top of the dolomite horizon in the Vulcan well is over 1400 ft. deeper than in Royalite No. 4 well, which is on the east anticline. McLeod No. 2 and Illinois-Alberta wells are on the west anticline, and although in each the top of the dolomite is somewhat deeper than in Royalite No. 4 well, the Illinois-Alberta well was finished at less than 3900 ft. depth. From

[1] Published with the permission of the Director, Geological Survey of Canada. Paper received April 18, 1927.

[2] *Journ. Inst. Petr. Techn.*, 1926, **12**, (57), 420-423.

[3] Mineral Production of Canada, Report of Dominion Bureau of Statistics, Feb., 1926.

present information, therefore, it is concluded that the porosity of the productive horizon has been proven for more than a mile along the strike of the anticline and on both the east and west subsidiary anticlines of the main anticlinal structure, and in no direction have the limits of porosity or productivity been attained. In the hope that the porosity continues throughout the length of the Turner Valley structure, wells are being drilled in a north-west and south-east direction over a distance of 12 miles.

Further geological investigations by the Geological Survey during the summer of 1926 has led to the conclusion that the northern end of the Turner Valley structure is cut off by a transverse fault with downthrow to the north. South of this transverse fault the structure is anticlinal, whereas to the north it is a westward-dipping fault block with a strike fault on the eastern side. One well—the Seneca—is now being drilled on the fault block at the northern end of Turner Valley, and since a large number of structures in the foothills are of the fault block type this well is of particular importance not only in relation to production on the fault block extension of Turner Valley but also in relation to many other structures in various parts of the foothills. A number of fault blocks structures comparable to that on which the Seneca well is being drilled are known in the foothills, and in many instances it will be possible to start drilling on much lower horizons than in Turner Valley. Successful completion of the Seneca well, therefore, will greatly increase the prospects of other areas in the foothills, where on account of limited knowledge concerning the relationship of oil to the structure, recommendations are at present somewhat hazardous.

Outside of Turner Valley, where 25 to 30 wells were being drilled in 1926, a few tests were under way in various parts of the foothills. In the northern foothills the Coalspur well, of the Imperial Oil Company, was abandoned at a depth of 4305 ft. without any prospects for production having been secured. Several wells were being drilled south of Bow River, but no well has yet been completed. These include tests in the Jumpingpound and Moose Mountain areas and on Morley Indian Reserve, all north-west of Turner Valley area and the Rice Creek area to the south.

In the Plains area, Roth No. 1 well, which was drilled in the Medicine Hat gas field, obtained gas in the Medicine Hat gas sand, but no further commercial production of oil or gas at greater depth. The well has been abandoned except as a gas well, and No. 2 well is being drilled. The Imperial Oil Company's Burdett well, which is being drilled on the Bow Island structure, found an oil sand in the lower Cretaceous, but a test of the well failed to give commercial production and the well is being deepened.

In eastern-central Alberta the Imperial Ribstone No. 1 well, drilled on the structure outlined by the Geological Survey in 1925, on Battle River close to the Alberta-Saskatchewan boundary, obtained a considerable flow of gas at about 1400 ft. depth. Between 1870 and 1900 ft. an oil sand was encountered and tested, but yielded only 4 to 5 barrels per diem of 18° Baumé oil. The well is being deepened, and at the time of writing is several hundred feet into the Palæozoic limestone underlying the Cretaceous. Two other wells are now being drilled on this favourable structure, and it would appear that their prospects depend on finding a more effective porosity within the oil sand and a gas pressure sufficient to drive the oil into a well.

In the Ontario field, according to a communication from the Natural Gas Commissioner, "there have been no new discoveries made in 1926, and all exploratory work has given negative results." It is understood the Imperial Oil Company have optioned practically the entire Bothwell field in Kent county with a view to mining the oil sands by the Ranney process. A number of diamond drill holes have been bored to test the character and thickness of the oil sands, but no results are available for publication.

British West Indies.*

By A. P. Catherall, B.Sc., M.I.Min.E., A.M.Inst.M.M. (Member).

Trinidad.

The period under review has been marked by steady progress in the proven fields of the Colony, and, as before, the greater part of the output of crude oil has been obtained from the Fyzabad-Morne L'Enfer-La Brea districts from which an increasing production is being obtained. The past year, however, has been marked by considerable activity in new areas, the chief of which are Palo-Seco-Erin, Cedros and Guayaguayare. In all these areas the results have been promising and it is hoped in the near future an increased production will be obtained.

The following table will show the number of feet drilled and the quantity of oil produced during 1926 as compared with the years 1924 and 1925 :—

* Paper received March 26, 1927.

	Year ended Dec. 31st, 1924.		Year ended Dec. 31st, 1925.		Year ended Dec. 31st, 1926.	
	Feet drilled.	Oil won. Barrels of 35 galls.	Feet drilled.	Oil won. Barrels of 35 galls.	Feet drilled.	Oil won. Barrels of 35 galls.
Crown Lands	97,039	2,486,269	105,631	2,877,437	126,330	2,976,227
Private Lands	54,853	1,570,343	63,522	1,509,070	73,239	1,995,243
	151,892	4,056,612	169,153	4,386,507	199,569	4,971,471

During the year under review 127 wells were drilled, of which 81 were on Crown Lands and 46 on private lands. In 77 of these wells oil was struck. The total number of wells drilled in the Colony to December 31st, 1926, is 1154.

The exports of petroleum products show a large increase compared with last year, the figures being 139,500,000 gallons, valued at £1,871,851 as against 26,000,000 gallons valued at £1,560,000 during 1925. The major portion of the export trade is in the form of fuel oil of which a large part is shipped to the Admiralty under contract.

There have been no new shipping or refining depots constructed during the period under review, which remain the same as last year, viz. :—

Claxton Bay: Trinidad Central Oilfields, Limited.
Pointe-a-Pierre: Trinidad Leaseholds, Limited.
Brighton: Trinidad Lake Petroleum Company, Limited.
Point Fortin: United British Refineries, Limited.

The Trinidad Leaseholds, Ltd., has made very considerable additions to its refining depot at Pointe-a-Pierre by the addition of a Dubb's cracking plant for the treatment of fuel oil. At the close of the year it was nearly complete and at the time of writing had just been put into operation. A very considerable extension to the pier of the Trinidad Lake Asphalt Operating Co., Ltd. (with which is associated the Trinidad Lake Petroleum Co., Ltd.) at Brighton has been made.

The following is a brief summary of the operation of the oil companies working in the Colony.

Trinidad Leaseholds, Limited.—Largest producing company in the Colony. Large purchases of crude oil are made from other companies and refined at Pointe-a-Pierre. The fields at Fyzabad and Barrackpore have been considerably extended. Drilling has been recommenced at Guayaguayare and preparations commenced for an extensive drilling programme. A Dubb's cracking plant has been erected at Pointe-a-Pierre.

Apex (Trinidad) Oilfields, Limited.—Second largest producing company in the Colony. The production has been largely increased compared with former years.

United British Oilfields of Trinidad, Limited.—Drilling has been continued at Point Fortin, Parry Lands, and a small production continues to be obtained from the field at Los Bajos.

Trinidad Central Oilfields, Limited.—Wells have been drilled at Tabaquite, Guapo and Rio Claro, production being obtained from the two former fields. The production from the latter was so small that the whole field was abandoned.

Trinidad Lake Petroleum Company, Limited.—Producing only.

Petroleum Development Company, Limited.—Drilling on Crown oil rights near the Pitch Lake with very satisfactory results.

Kern Trinidad Oilfields, Limited.—Development of Perseverance Estate, Guapo, continued during the whole of the year. Operations were continued on Crown Lands near Guapo. A satisfactory production was obtained.

General Petroleum Company of Trinidad, Limited.—Little work was done by this company whose properties have now been acquired by the Trinidad Leaseholds, Limited.

Trinidad Petroleum Development Company, Limited.—The company has carried on drilling operations at Cedros, Palo Seco and Guapo. Production has been successfully obtained in the two former districts.

British Controlled Oilfields, Ltd.—Drilling operations have been suspended for some time past and small production has been obtained from existing wells.

Petroleum Options, Limited.—Produced from two wells and recommenced drilling towards the close of the year.

Trinidad Friendship Petroleum Company, Limited.—Drilled one well and produced from three.

W. B. S. Collie.—Lands formerly held by the Trinidad United Oilfields, Ltd. Two new wells were sunk.

Trinidad Oilfields Operating Company, Limited.—This company commenced a very active drilling programme towards the end of the year chiefly in new areas.

BARBADOS.

The British Union Oil Company, Limited, has continued development operations in this Colony, but so far production has not been obtained on a commercial scale.

BRITISH GUIANA.

No petroleum has yet been obtained in this Colony.

Shale-Oil Research in Estonia: Chemical Composition and Autoxidation of Light Distillates.*

By P. N. Kogerman, M.Sc., D.I.C., F.C.S. (Member).

General.—The competition on the world's oil-market has put a drag on the rapid development of shale-oil industry. The problem of a cheap and easy-to-operate retort for the very rich but somewhat "capricious" Estonian oil shale is still not satisfactorily solved. From the oil-man's point of view the crude shale-oils produced so far on commercial scale in producer-retorts are heavy and cannot compete with a good well-oil. It is therefore natural that the oil or shale technologist should use his efforts for solving the two main groups of problems: (i.) to work out a cheap retorting method, which produces a crude comparable with a good well-petroleum, and (ii.) to find the best refining method for the crude oils obtainable already at the existing retorting plants.

The first problem cannot be solved in the laboratory alone, but requires large sums of money for operating semi-large experimental plants; in spite of the difficulties considerable progress has been made in this direction.

The second problem requires a large amount of preliminary study in the laboratory, and it is this group of problems that has been attacked so far in the Oil Shale Research Laboratory at the University of Tartu. The laboratory was established in September, 1925; research work on the following problems has been carried out: (i.) the isolation and properties of phenols of shale-oil;[1] (ii.) utilisation of phenoxides from shale-oil for wood preservation;[2] (iii.) cracking of shale-oil;[3] (iv.) hydrogenation of shale and shale-oils; (v.) production of lubricating oils; (vi.) chemical composition of light shale-oils; (vii.) autoxidation of light distillates; (viii.) chemical composition of Manchurian (Fushun) shale-oil obtained in a Pintsch producer; (ix.) composition of oils, obtained by different methods of retorting, and some other problems.

Chemistry of light distillates.—The results of researches on chemical composition of light distillates and their autoxidation are of importance to every petroleum chemist, and a summary of the results is given in the notes below.

The light oil was obtained from the Kohtla crude oil[4] by steam distillation; its sp. gravity was 0·7726 at 15° C. and $n_D^{20}=1{\cdot}4319$.

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* Paper received June 15th, 1927.

[1] See P. N. Kogerman, *J.S.C.I.*, 1927, **46**, 138–143 T.

[2] N. Wiederpass and P. N. Kogerman, *Sitzungsber. Naturforsch.-Ges. Univ. Tartu*, 1926, **33**, (1). and *Brit. Chem. Abs.*, B., 747, 1926.

[3] N. Wiederpass, *Sitzungsber. Naturforsch.-Ges. Univ. Tartu*, 1927, **34**, (2).

[4] For particulars of the crude oil see this Journal, 1926, No. 57, p. 432.

A portion of the light oil was treated in the usual way: firstly with conc. sulphuric acid at 0° C., then with fumic sulphuric acid (containing 10 per cent. SO_3) at the same temperature, washed with dilute alkali and water, and refractionated. (Sp. gravity of the refined oil=0·723 at 15° C.) A three-bulb distillation head was used. After two refractionations only very slight differences were found in the amounts of individual fractions corresponding to equal intervals of temperature, but after about 40 refractionations the fractions "accumulated" at certain temperatures. For instance, the quantities of oil in c.c. per 2° C. intervals, beginning with 124° C. were as follows:—9·0; 20·1 (126–127° C.); 5·5; 2·2; 2·5; 1·7; 2·4; 4·0; 6·0; 8·3; 9·0; 8·2; 20·0; 9·3; 7·0; 4·2; 3·0, etc.

The large fractions were fractionated separately, and finally five fractions with fairly constant boiling points were obtained. The particulars of the analysis of these fractions are given in Table I.:—

TABLE I.

CONSTANTS AND COMPOSITION OF SATURATED HYDROCARBONS FROM SHALE-OIL.

	B. pts. ° C.	Sp. grs. at 20° C.	Refract. indices at 0·0° C.	Ultimate composition per cent. C.	H.	Formulas
1.	68·5–69·5°	0·6647	1·3775	—	—	C_9H_{14}
2.	98·5–99·5°	0·6933	1·3908	83·79	16·18	C_9H_{16}
3.	124–126°	0·7147	1·4018	83·99	15·97	C_9H_{18}
4.	148·5–149·5°	0·7323	1·4111	84·13	15·24	$C_{10}H_{20}$
5.	172·4–174°	0·7509	1·4198	84·32	15·67	$C_{12}H_{26}$

Thus in the light shale oil the normal saturated hydrocarbons (about 35 per cent. of the oil) predominate. About 26·0 per cent. of the oil was absorbed by conc. H_2SO_4 and about 10 per cent. was polymerized.

Another portion of the oil was treated with liquid SO_2 at −20° C. (Edeleanu's method) in order to isolate some unsaturated and cyclic compounds: 3500 c.c. of oil yielded about 950 c.c. of extract and about 2350 c.c. of refined oil.

Properties of the products are given in Table II.:—

TABLE II.

PROPERTIES OF OILS OBTAINED BY EDELEANU'S METHOD.

	Untreated oil.	Refined oil.	Extract.
Sp. grs. at 15° C.	0·7726	0·7567	0·8067
Refract. indices at 20° C.	1·4319	1·4235	1·4495
Per cent. of saturation (1 vol. of oil+1 vol. of conc. H_2SO_4)	73%	79%	59%
Colour	Orange	Yellow	Ruby-red

This research is a very delicate one and requires long time for completion. On the basis of experimental data available the presence of naphthenes (derivatives of *dihydro-* and *tetrahydro-benzenes*) is assumed.

Autoxidation and gum formation.—About 3 litres of the untreated light oil was carefully refractionated into 2–5° C. fractions and allowed to stand in corked glass flasks for about 18 months. After about six months the formation of condensation or polymerisation products ("gums") was noticed in certain fractions, these fractions were: 90–92° C., 98–100° C., 107–108° C., and 110–111° C. The condensation (resp. oxidation) products were insoluble in the bulk of the oil and formed amber-yellow heavy layers on the bottom of the flasks, they are similar to the fluid resin which forms in cracked gasoline on exposure to air.[5] The amount of fluid resin or "gum" in certain fractions reached up to 10 per cent. of the weight of the fraction. The gum formation was limited only to the middle fractions of the light oil, *i.e.*, 90°–125° C. The higher fractions showed no deposit of gum, although the colour darkened considerably on standing: from yellow to orange-red. It is noteworthy that the darkening of colour in some cases did not effect the indices of refractions: for instance the fraction b.p. 162–163° C. is yellowish-brown, sp. gravity=0·7908 at 20°, refr. ind.: n_D^{20}=1·4417 the fraction b.p. 163–164° C. is yellow, sp. gravity=0·7911 and refr. ind. n_D^{20}=1·4417.

The colour of the fractions between the fractions with the gum-deposit remained practically water white. The fluid resins were very viscous. The Table III. gives some constants of the oil and resins:—

TABLE III.

PROPERTIES OF OILS AND FLUID RESINS FORMED ON OXIDATION OF SHALE-OIL.

		Oil		Fluid resin		Per cent. of resins by wt. of the fraction.
B. pts. ° C.	Colour.	Sp. gr. at 20° C.	n_D^{20}	Sp. gr.	n_D^{20}	
90–92°	Pale yellow	0·7393	1·4077	—	1·4719	4·2
98–100°	" "	0·7516	1·4141	1·0531 at 20°	1·4730	—
107–108°	" "	0·7637	1·4178	1·0538 at 16°	1·4742	10·1
109–110°	Water white	0·7382	1·4158	No gum formed		—
110–111°	Pale yellow	0·7726	1·4207	1·0308 at 17·5°	1·4702	10·5

The ultimate analysis of the fraction b.p. 107–108 gave for the oil: C, 82·13 per cent., H, 13·48 per cent., S, traces, oxygen (from difference) 4·39 per cent., the so-called "gum" contained: C, 61·38 per cent., H, 9·20 per cent., S, 0·47 per cent. and

[5] B. T. Brooks, *Ind. and Eng. Chem.*, 1926, **18**, 1199.

O_2 (diff.) 28·95 per cent. So the formation of a fluid resin is dependent upon the oxidation of the light distillates. B. T. Brooks and J. W. Humphrey[6] suggested that "diolefines are probably the cause of the resinification which has been observed when highly cracked gasolines are permitted to stand for several months." The oxidation seems to proceed in stages: firstly organic peroxides[7] are formed; then the peroxide decomposes with the formation of aldehydes or dialdehydes; some organic acids are formed of course. A qualitative study of the shale oil gums showed the presence of peroxides, aldehydes and acids.

After standing for about twelve months in four fractions (*i.e.*, b.pts. 94–96° C., 104–105° C., 109–110° C. and 117–118° C.) the formation of white, needle-like *crystals* was observed. No gum formation was observed in these fractions previously, nor did the colour darken. The crystals were soluble in water, the solution was strongly acid (reaction with litmus), m.p. about 87° C. Average mol. wt. was 134. Micro-combustion of the crystals gave the following figures for hydrogen and carbon: C, 61·30 per cent., H_2, 10·44 per cent., which corresponds to an empirical formula $(C_3H_6O)_n$. Taking into consideration the mol. wt., the crystals seem to be a mixture of an aldehyde and of an acid or an aldehyde acid.

The evaporation of the fraction *in vacuo* did not increase the amount of the crystals. The crystals sublime on heating.

[6] Brooks and Humphrey, *J. Am. Chem. Soc.*, 1918, **40**, 852. Brooks and Parker, *Ind. and Eng. Chem.*, 1924, **16**, 587.

[7] Brooks, *loc. cit.* Compare J. N. Friend: "Chemistry of Linseed Oil," London, 1917, p. 70.

World's Production of Crude Petroleum.

By GEORGE SELL (Associate Member).

According to the figures at present available, the total world's production of crude petroleum, exclusive of shale oil, during 1926 amounted to 152,110,500 metric tons. Compared with the previous year this figure shows an increase of 3,614,000 metric tons, or about 2·4 per cent.

The table given below shows the quantities produced by the various countries for the years 1925 and 1926 and is based, as far as possible, on official returns. In many cases the final details are not yet available and estimates have had to be made according to preliminary returns.

WORLD'S PRODUCTION OF CRUDE PETROLEUM.

Country.	1925. Quantity. Metric tons.	1925. Percentage of total.	1926. Quantity. Metric tons.	1926. Percentage of total.
United States ..	104,622,000	70·454	106,000,000	69·686
Mexico	17,600,000	11·852	13,750,000	9·039
Russia	7,295,000	4·912	8,500,000	5·588
Venezuela	2,884,000	1·942	5,420,000	3·563
Persia	4,652,000	3·133	4,750,000	3·123
Rumania	2,316,500	1·560	3,256,400	2·141
Dutch East Indies ..	3,066,100	2·065	3,152,000	2·072
Peru	1,270,000	0·855	1,500,000	0·986
Argentina	874,300	0·589	950,000	0·625
Colombia	135,000	0·091	864,000	0·568
Poland	812,000	0·547	796,000	0·523
Japan	280,000 ..	0·189	266,000	0·175
Egypt	178,600	0·120	171,000	0·112
Germany	55,000	0·037	96,000	0·063
France	64,900	0·043	76,000	0·050
Ecuador	19,000	0·013	37,000	0·024
Czecho-Slovakia ..	10,000	0·007	10,000	0·007
Italy	7,500	0·005	8,000	0·005
Algeria	1,800	0·001	1,400	0·001
British Empire:				
India	1,100,000	0·741	1,155,000	0·760
Trinidad	585,000	0·394	663,000	0·436
Sarawak	613,000	0·413	633,000	0·416
Canada	44,800	0·030	45,700	0·030
Other countries ..	10,000	0·007	10,000	0·007
Total	148,496,500	100·000	152,110,500	100·000

From the above table it will be seen that the largest increases in production have been in South America. Both Venezuela and Ecuador have practically doubled the figures for the previous year and Colombia has increased from 135,000 metric tons in 1925 to 864,000 metric tons in 1926.

The total production of crude petroleum in the British Empire amounted to 2,496,700 metric tons in 1926, compared with 2,342,800 metric tons in 1925, an increase of 153,900 metric tons, or about 6·5 per cent. Expressed as a percentage of the total world's production, the British Empire produced about 1·65 per cent. in 1926 and about 1·58 per cent. in 1925.